JOURNAL OF CATALYSIS **43**, 122–130 (1976)

Adsorption and Interaction of C_2H_4, H_2, CO, and Organic Acids on Fe, Co, and Ni

G. BLYHOLDER, D. SHIHABI, W. V. WYATT,[1] AND R. BARTLETT

Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701

Received September 11, 1975

Infrared spectra for the surface species formed by the adsorption and interaction of C_2H_4, H_2, and CO on silica-supported Co and Ni have been obtained. Initially ethyl groups are formed on the surfaces. When the gaseous mixture is heated to 100°C over Co a new surface reaction is observed, namely the formation of surface complexes with a carboxylate structure. The mechanism of the interaction of chemisorbed CO and ethyl groups to form the surface carboxylate is discussed in terms of alkyl migration reactions which are similar to the homogeneous coordination complex reactions in hydroformylation catalysis. The surface species and alkyl migration reactions are proposed to also be important in CO methanation and Fischer-Tropsch synthesis. The infrared spectra of formic, acetic, and propionic acids adsorbed on Fe, Co, and Ni indicate the formation of surface carboxylate species. The asymmetric carboxylate stretch in the 1550 to 1600 cm^{-1} region shifts to lower frequencies as the number of carbon atoms in the adsorbed acid increases. The surface carboxylates are stable at temperatures up to 150 to 200°C.

INTRODUCTION

Despite the large amount of study that the interaction of organic molecules with metal surfaces has received because of its industrial importance and an intrinsic interest in understanding catalytic processes, relatively little is definitely known about the reactions of organic molecules while they are on the surface and almost everthing has been postulated to occur. It is our aim to reduce the uncertainty by determining the initial structure of adsorbed molecules using infrared spectroscopy and to follow their reactions while still on the surface to form other surface species. Analogies to homogeneous reactions in coordination complexes will be found to be useful in discussing the observed reactions. Although such analogies have often been proposed there have been so few data dealing directly with reactions among surface species that few direct comparisons of homogeneous and heterogeneous processes have been possible.

The insertion reaction of CO into a metal–alkyl bond is reasonably well characterized (*1–3*) as a coordination complex reaction and has been shown (*4*) to occur on a Fe surface during the interaction of CO and C_2H_4. Here the interaction of CO and C_2H_4 are examined on Co and Ni surfaces. The structure of adsorbed CO on Fe, Co, and Ni surfaces has received sufficient attention to characterize the surface complex (*5–9*). The adsorption of ethylene on Ni has been looked at by several groups (*5, 10–13*) and suggested to produce surface butyl groups (*10–13*). Our work here does not entirely concur with this conclusion. Ethylene adsorption on Co has been studied (*14*) with a low resolution infrared spectrometer and so

---

[1] Present address: Department of Chemistry, Arkansas State University, State College, Ark.

will be reexamined in more detail here. The formation of organic acids on the surface became important in this work. Since infrared spectra of only formic acid on metal surfaces have been previously reported (*15*) a systematic investigation of the infrared spectra of formic, acetic and propionic acids on Fe, Co, and Ni is also reported here.

EXPERIMENTAL SECTION

The adsorption of C_2H_4 and the interaction of CO and C_2H_4 were carried out on silica-supported Co and Ni. The experimental technique, cells and sample preparation were similar to those used previously (*16*). The KBr infrared windows were sealed to the reaction cell with o-rings. The silica-supported metals were prepared by making a slurry of the hexahydrate of either cobalt or nickel nitrate (J. T. Baker, reagent) with Cab-O-Sil, M5 (G. L. Cabot Co.) so that an ultimate composition of 9% metal and 91% silica was produced. The slurry was dried at 100°C and powdered. Approximately 80 mg of the powder was pressed into a 2.5 cm diameter disk. Reduction of the metal nitrate in the disk was carried out in the infrared cell by a flow of dry, oxygen-free H_2 at 430°C for 14 hr. The spectra were recorded over the range 4000–1300 cm^{-1} on a Perkin-Elmer model 457 spectrophotometer using a pure silica disk in the reference beam. The adsorbates were purified by evacuation during several freeze–thaw cycles and fractional distillation.

The spectra of the adsorbed acids were obtained using the technique, which has been described in detail elsewhere (*17*), consisting of evaporating a metal from an electrically heated tungsten filament in the presence of a small pressure of helium. The metal particles formed in the gas phase deposit in a hydrocarbon oil film on the salt windows of an infrared cell. The gas to be studied is admitted to the cell and the spectra of chemisorbed species are recorded. Spectra are recorded before and after admission of the gas to the cell. Five minutes pumping has been found sufficient to remove spectra due to gas phase molecules. This technique has the advantage that a wide spectral range is available for study. The oil is apparently only weakly adsorbed on the metal particles since many gases have been found to chemisorb readily on the metal and spectra like those obtained by other techniques have been found where comparisons are possible.

RESULTS AND SPECTRAL ASSIGNMENTS

Spectra obtained for C_2H_4 adsorbed on silica-supported Ni at 25°C under varying conditions of H_2, evacuation and CO addition are shown in Fig. 1. The bands are assigned (*18, 19*) as follows:

3023 cm^{-1}	$=CH-$ str.
2962	CH_3 asym. str.
2930	CH_2 asym. str.
2880	CH_2 and CH_3 sym. str.
2860sh	

The addition of CO at 25°C to the chemisorbed ethylene shifted the bands about 10 cm^{-1} to higher frequencies as shown in spectrum e. Evacuation for 18 hr did not further reduce the intensities of the C–H bands. Heating for 23 hr with 2.5 cm of D_2 at 90°C slightly reduced the C–H intensities and produced no C–D band. Further heating for 24 hr with 2.5 cm of D_2 at 150°C removed the C–H bands entirely and produced no C–D bands.

The difficulty in removing the hydrocarbon species from the above surface which had undergone several heat treatments and had CO chemisorbed is in distinct contrast to the ease of removal of hydrocarbon species shortly after adsorption. When a fresh sample had C_2H_4 and H_2 adsorbed, a spectrum similar to spectrum b of Fig. 1 was produced except that the 2930 cm^{-1} was a little less intense than the 2960 cm^{-1} band. Heating this sample

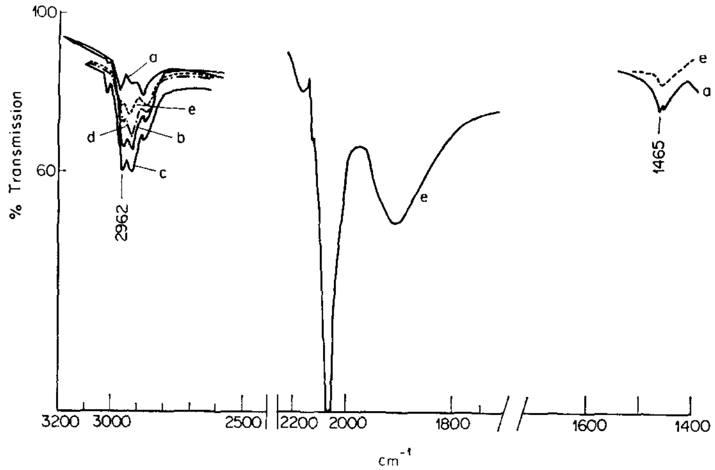


FIG. 1. Spectrum of ethylene chemisorbed on Ni at 25°C. (a) Gas phase ethylene evacuated; (b) after adding H_2; (c) after heating for one hour at 80°C; (d) cell degassed; (e) addition of CO.

for 8 hr at 70°C in 6 cm of D_2 completely removed the C–H band and produced only a small band (less than 10% of the area of the original C–H band) in the C–D stretching region.

To assist in making band assignments in this and future work a spectrum of ethylene-D_4 on a D_2 covered Ni surface at 25°C was recorded and is shown in Fig. 2. The bands are assigned as follows (*20, 21*):

2265 cm^{-1}	CD_4 gas
2230	CD_3 asym. str.
2210sh	
2120	CD_3 and CD_2 sym. str.

Adsorption of C_2H_4 and H_2 on silica-supported Co produced spectra very similar to those for Ni shown in Fig. 1. The ratio of the intensity of the 2960 cm^{-1} band assigned to a CH_3 stretch to the 2930 cm^{-1} band assigned to a CH_2 stretch varies about 20% from one sample to another and with addition of H_2 or evacuation.

Adsorption of C_2D_4 and D_2 on silica-supported Co produces spectra very similar to those in Fig. 2 for Ni.

For comparison purposes in discussing possible structures of adsorbed species the spectrum of *cis*-2-butene adsorbed on silica-supported Co at 25°C was obtained and is shown in Fig. 3. The band maxima occur at 2970, 2930 and 2880 cm^{-1}.

After 10 cm of an equimolar mixture of C_2H_4, H_2, and CO is admitted over silica-supported Co and heated to 100°C for 20 hr the spectrum of the surface species following evacuation at 25°C is as shown in Fig. 4. As well as the usual collection of bands near 2900 cm^{-1} for C–H stretching

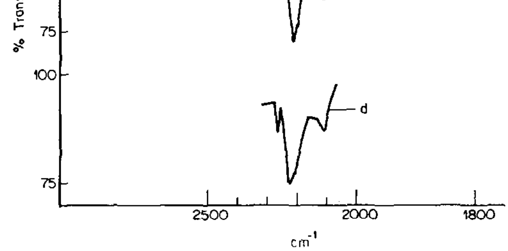


FIG. 2. Infrared spectrum of ethylene-d_4 chemisorbed on D_2 covered Ni at 25°C. (a') Background; (a) spectrum of chemisorbed ethylene; (b) after adding D_2; (c) long time contact with D_2 gas; (d) heating with D_2 at 80°C for 1 hr.

motions, bands at 2020 and 1830 cm^{-1} for chemisorbed CO, and a band at 1460 cm^{-1} for CH_3 and CH_2 deformation motions, there are two strong bands at 1557 and 1435 cm^{-1} which may be assigned to the asymmetric and symmetric stretch of an organic carboxylate group with more than 3 carbon atoms on the basis of the following data.

In order to make more definite the assignment of infrared bands to organic carboxylate structures on metal surfaces the infrared spectra of formic, acetic and propionic acids adsorbed on iron, cobalt and nickel were obtained and are given in Table 1. In all cases the spectra of the surface species obtained after a 45 min evacuation of the cell are very similar to those of the carboxylate anions (*22–26*) so the band assignments are those of the ions and the structure of the predominate surface species is presumed to be a bidentate coordination of a carboxylate group to a surface metal atom.

The sodium salts of acetic, propionic and 2,2-dimethyl propionic acids have asymmetric carboxylate stretches (*27*) at 1583, 1565, and 1551 cm^{-1}, respectively; thus indicating a decrease in this frequency as the number of carbon atoms increases. The data of Flett (*28*) gives frequencies a few wavenumbers different from the above but for the sodium salts of acetic, propionic and butyric acids shows the same trend. Probably due to packing interactions in the solid state for its small ions sodium formate does not fit into this series but the frequency of the aqueous formate ion (*23*) at 1585 cm^{-1} does fit into theseries. The data in Table 1 for carboxylate species on Fe, Co, and Ni all show a decrease in the asymmetri ccarboxylate stretching frequency as the number of carbon atoms increases. On the basis of this progression the band at 1557 cm^{-1} in Fig. 4 is assigned as stated in the second paragraph above to a carboxylate group with more than 3 carbon atoms.

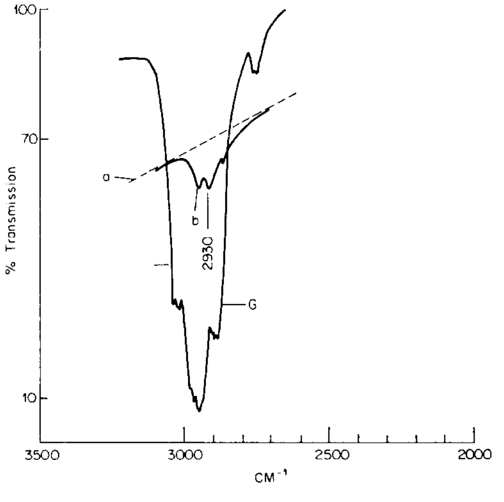


FIG. 3. Infrared spectrum of *cis*-2-butene on Co. (a) Background; (G) gas phase spectrum; (b) gas phase degassed and H_2 added.

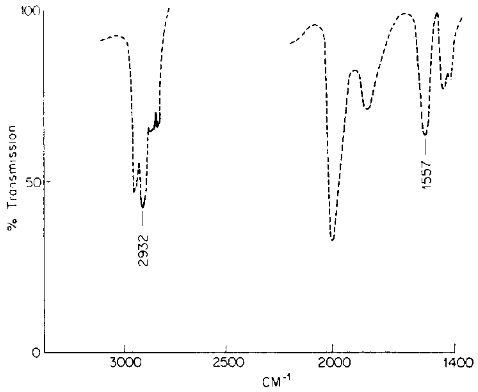


FIG. 4. The infrared spectrum resulting from the interaction of ethylene, carbon monoxide, and hydrogen with a silica supported cobalt surface at 100°C (gas phase was degassed).

In obtaining the spectra of the chemisorbed acids the surface was exposed to 8 mm of formic or acetic acid or 3 mm of propionic acid for 45 min before evacuation. In order to see if there were still open sites on the surface, 10 mm of CO was admitted to each cell for 30 min at this stage. On Fe with adsorbed formic or acetic acid, no bands for chemisorbed CO appeared while with propionic acid a weak band for chemisorbed CO appeared. For all three acids on Co and Ni a medium intensity band for chemisorbed

TABLE I

Infrared Fequencies and Assignments for Formic, Acetic, and Propionic Acids Adsorbed on Fe, Co, and Ni

Fe	Co	Ni	Na formate	Assignments
Formic acid				
1580	1580s	1580s	1567s	O–C–O asym. str.
1350s	1350m	1345s	1350s	O–C–O sym. str.
775m	780m	790m	772m	O–C–O bend
Acetic acid			Na acetate	
		1690w		
1575s	1580s	1575s	1578s	O–C–O asym. str.
			1498vw	CH_3 def.
			1443sh	CH_3 def.
1440s	1450s	1410s	1430s	O–C–O sym. str.
			1414sh	CH_3 def.
1340w	1350sh	1340w		
1045vw		1045w	1042w	CH_3 rock
1020w	1020w	1020m	1009w	CH_3 rock
		940w	924w	C–C str.
660m	670w	670m	646m	O–C–O def.
610w		620w	615w	O–C–O def.
Propionic acid			Na propionate	
		1680sh		
1560s	1570s	1570s	1565s	O–C–O asym. str.
			1460s	C–H def.
1425s	1425m	1410s	1420m	O–C–O sym. str.
1290m	1295m	1290m	1350m	
	1240sh	1240sh		
1080m	1080m	1080m	1080w	
	1010w		1000w	
885w	890w	885m	880m	
805w	800w	810w	810m	
		670w	720w	

CO was produced. The intensity was about one-fourth of the intensity usually produced by CO on a freshly evaporated sample.

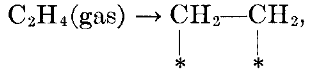
In order to get a rough idea of the stability of the carboxylate structure on the surface, after the gas phase CO was evacuated 20 cm of H_2 was added and the cell heated to 100°C for 30 min, a spectrum recorded, the cell was then heated to 150°C for 30 min, a spectrum recorded, and finally the cell was heated to 200°C for 30 min and a spectrum recorded. On Fe the formate bands persisted unchanged until removed by the 200°C treatment, the acetate bands were still at about one-half their original intensity after the 200°C treatment and medium intensity bands for acetic acid were present at 200°C after having first appeared at 150°C, and the propionate bands were only reduced moderately at 200°C. On cobalt the formate bands were reduced a little at 150°C and had almost disappeared at 200°C, the acetate bands were little changed as 200°C although weak bands for the free acid appeared and at 200°C the propionate bands were mostly gone. On Ni the formate bands disappeared during the 200°C treatment while the propionate bands showed no change after the 200°C treatment.

DISCUSSION

The most interesting and important finding in this work is that CO, C_2H_4, and H_2 will interact at 100°C on a metal surface to produce a surface carboxylate species. No surface reaction like this has been previously indentified although mechanistic considerations lead to the suggestion that it is closely related to some homogenous coordination complex reactions and the catalytic hydroformylation reaction. Before discussing the mechanism the surface carboxylate product and the initial surface species need to be considered carefully.

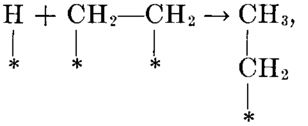
Since the silica support obscures the spectral region below 1300 cm^{-1}, an adsorbed carboxyate group only gives group frequencies for C–H bonds and the carboxylate group. However, the evaporated metal technique allows the region below 1300 cm^{-1} to be investigated for skeletal vibrations which are characteristic of particular organic acids. The close correspondence in Table 1 between the skeletal and carboxylate group frequencies of the adsorbed organic acids and the corresponding carboxylate ions indicates that the organic acids are adsorbed by loss of the acid hydrogen so that the carboxylate group coordinates with the surface and that the skeletal structure does not dissociate upon adsorption. The heating experiments show that the carboxylate structure is quite stable on Fe, Co and Ni surfaces since it was not changed until the cell was heated to 150 to 200°C and not even then in some cases. At the 100°C temperature at which carboxylate formation was observed from CO, C_2H_4 and H_2, these results from organic acid adsorption certainly indicate that the carboxylate group is stable on metal surfaces. The observation of the two bands at 1557 and 1435 cm^{-1} in Fig. 4 reasonably certainly indicates carboxylate formation on the silica-supported cobalt. As the number of carbon atoms increases in carboxylate ions the asymmetric stretch between 1550 and 1600 cm^{-1} decreases in frequency. The data in Table 1 indicates that this trend is maintained in the surface carboxylate groups. The band at 1557 cm^{-1} for the carboxylate species on silica-supported cobalt would then represent a group with more than 3 carbon atoms.

The spectrum of ethylene and hydrogen adsorbed on metals has been interpreted in terms of various structures illustrated below where a bond to a metal atom is represented by an asterisk.



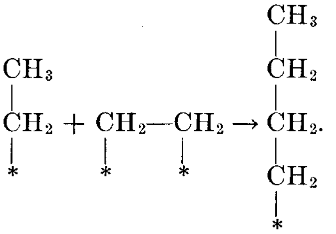
$$\mathrm{C_2H_4(gas)} \rightarrow \underset{\overset{|}{*}}{\mathrm{CH_2}}\!-\!\underset{\overset{|}{*}}{\mathrm{CH_2}},$$

(1)



$$\underset{\overset{|}{*}}{\mathrm{H}} + \underset{\overset{|}{*}}{\mathrm{CH_2}}\!-\!\underset{\overset{|}{*}}{\mathrm{CH_2}} \rightarrow \begin{array}{c}\mathrm{CH_3,}\\ | \\ \mathrm{CH_2} \\ | \\ * \end{array}$$

(2)



$$\begin{array}{c}\mathrm{CH_3}\\ | \\ \mathrm{CH_2} \\ | \\ * \end{array} + \underset{\overset{|}{*}}{\mathrm{CH_2}}\!-\!\underset{\overset{|}{*}}{\mathrm{CH_2}} \rightarrow \begin{array}{c}\mathrm{CH_3}\\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CH_2.} \\ | \\ \mathrm{CH_2} \\ | \\ * \end{array}$$

(3)

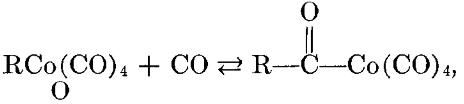
There is a question as to the relative number of butyl vs ethyl groups on the surface. Several authors (*10–13*) have suggested that butyl groups predominate on the basis of comparing the spectra of the adsorbed species produced from C_2H_4 and H_2 with the spectrum of adsorbed butene-1 and H_2 which presumably produces an adsorbed butyl group. Comparison of Figs. 1 and 3 demonstrates the basis for this argument. This argument is usually accompanied by the statement or implication that the ratio of CH_3 to CH_2 groups can be determined by the ratio of the 2960 cm^{-1} band (asym. CH_3 str.) to the 2930 cm^{-1} band (asym CH_2 str.). While such use of this ratio may well be legitimate for a series of similar compounds differing only in carbon chain length, the spectra in Fig. 2 of Sheppard and Ward (*29*) show the ratio of the 2960 to 2930 cm^{-1} band varying by a factor of 2 as an ethyl group is placed in different bonding situations. Further this figure which includes butyl groups shows that there is no unique pattern that will always distinguish ethyl from butyl groups when the nature of the bonding situation is changed. One may also note that the intensity pattern in the C–H region in Fig. 1 of our work changes greatly as hydrogen treatment and evacuation change. One can also ask whether it is possible to distinguish between an adsorbed butyl group and an adsorbed ethyl group plus an associatively adsorbed ethylene molecule since the CH_3/CH_2 ratio would be the same. This distinction would not be clear provided that the band positions were not greatly affected by bonding to the metal. Morrow (*30*) has shown that the band positions are shifted for an ethyl group in a triphenylphosphine Pt complex and so supports the formation of butyl groups from C_2H_4 on Ni. However, the spectra in Fig. 2 of Sheppard and Ward (*29*) do not show appreciable shifts for ethyl groups bonded to Sn or Fe. This seems to leave the situation that butyl groups may certainly exist on the surface but are not proved to exist to the exclusion of ethyl groups.

The spectra for C_2D_4 and D_2 adsorbed on Ni (shown in Fig. 2) and Co (similar but not shown) support the existence of ethyl groups on the surface. The spectrum (*20*) of $B(CD_3)_3$ has a closely spaced doublet with the more intense peak at 2230 cm^{-1} assigned to C–D stretching frequencies. The spectrum (*20*) of $B(C_2D_5)_3$ has in addition to the 2230 absorption a band of about one-half its intensity around 2100 cm^{-1} which is presumably primarily due to the CD_2 group. In the spectrum (*31*) of n-C_8D_{18}, which may be considered to be two butyl groups, the 2100 cm^{-1} band has about the same peak height as the 2230 cm^{-1} absorption. If we assume that the ratio of these two bands can be taken as a measure of the CD_3/CD_2 ratio then the spectra in Fig. 2 indicate adsorbed ethyl groups. This line of reasoning is based on a minimal amount of C–D data and makes the assumption that C–D intensities are less subject to environmental influences than C–H intensities.

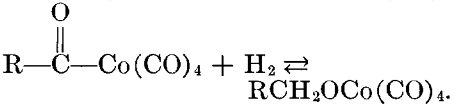
Since the inferences from C–H and C–D intensities about the existence of surface ethyl groups are not entirely above reproach one would like data from skeletal vibrations. The infrared spectrum of C_2D_4 and D_2 adsorbed on Fe (*4*) is just like that of Fig. 2. This material on Fe, which has been assigned as ethyl groups, has been shown (*4*) to react with CO to give chemisorbed isopropoxide groups which are identified by their skeletal vibrations in the 800 to 1200 cm^{-1} region. If the material on Fe had polymerized to butyl groups the reaction with CO should have produced a C_5 alkoxide. However, the skeletal vibrations of none of the possible C_5 alkoxide isomers are compatible with the observed spectra. This is taken as good evidence that spectra like those in Fig. 2 can reasonably be assigned to ethyl groups.

Having established that the most probable starting place is chemisorbed ethyl groups and CO and that the product is a surface carboxylate group with more than 3 carbon atoms, we are in a position to discuss mechanism. In the hydroformylation and related reactions involving homogeneous catalysis by cobalt carbonyls the following reactions are among those that appear to account well for the observed results (*32, 33*).

$$HCo(CO)_4 + C_2H_4 \rightarrow C_2H_5Co(CO)_4, \quad (4)$$

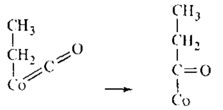


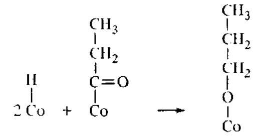
$$RCo(CO)_4 + CO \rightleftarrows R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}Co(CO)_4, \quad (5)$$

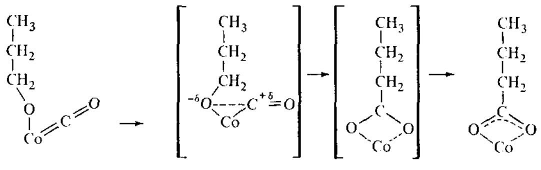


$$R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}Co(CO)_4 + H_2 \rightleftarrows RCH_2OCo(CO)_4. \quad (6)$$

With manganese carbonyls reactions like (5) have been shown to proceed via migration of the alkyl group to an existing CO ligand (*1–3*). By analogy to these homogeneous processes the following mechanism is proposed for carboxylate formation on the colbalt surface. The formation of a surface ethyl group may be either through the two step process shown in reactions (1) and (2) or by the direct interaction of C_2H_4 with a surface hydride in analogy to reaction (4).


(7)


(8)


(9)

Reactions (7) and (8) are the direct surface analogies of homogeneous reactions (5) and (6). The reverse of reactions (7) and (8) have been shown to occur on Co and Ni surfaces since adsorption of alcohols leads to some formation of acyl groups and chemisorbed CO (*34–36*). Reaction (8) appears to occur on Co and Fe since adsorption of acetaldehyde produces surface ethoxide structures (*35, 37*). This leaves only reaction (9) as not having direct precedents but alkyl migrations are well known and the 4 carbon carboxylate product structure is in agreement with the spectral data. The real test of this proposed step will come in seeing if alcohols which are known to adsorb with an alkoxide structure, will react with CO to produce a carboxylate structure. This will be the subject of a future communication.

Having found a new surface reaction, in this case carboxylate formation from CO, C_2H_4, and H_2, the question of its generality arises. No evidence of carboxylate formation was found upon heating to 150°C a Ni surface with chemisorbed CO and alkyl groups. Previously reported spectra (*38*) for the surface species formed by the interaction of CO and H_2 at 180°C on silica-supported Fe show bands at 1560 and 1440 cm^{-1}. These bands were not interpreted at the time but now it seems most likely that they are due to a surface carboxylate. Thus the carboxylate formation reaction is found on Fe and Co but not Ni.

It would seem likely that the types of surface species and reactions found here are important in the methanation of CO and the Fischer-Tropsch reaction catalyzed on metals. The reaction products would be controlled by the relative rates of alkyl group migration and hydrogenolysis of particular bonds. Ni is a good catalyst for the CO methanation reaction but a poor Fischer-Tropsch catalyst. This work indicates that an alkyl group does not readily migrate from an alkoxide group to a chemisorbed CO on a Ni surface. Hydrogenation of a surface methoxy group formed by hydrogenating CO on a Ni surface would then give CH_4. Fe and Co are often good Fischer-Tropsch catalysts. Alkyl migration has been shown here to readily occur from an alkoxide species to a chemisorbed CO molecule. If the hydrogen activity is such that the oxygen from the alkoxide is hydrogenated to water rather than becoming part of a carboxyl group, an acyl is formed which may be readily hydrogenated to any alkoxide which is one carbon atom longer than previously. Thus chain growth can occur in the Fischer-Tropsch reaction by reactions like those proposed herein. Clearly more work needs to be done in characterizing surface species and their reactions, particularly with respect to alkoxides, but it appears that a foundation has been laid for understanding the surface species involved in CO methanation and the Fischer-Tropsch synthesis.

REFERENCES

1. Heck, R. F., and Breslow, D. S., *J. Amer. Chem. Soc.* **84**, 2499 (1962).

2. Adkins, A., and Krsek, G., *J. Amer. Chem. Soc.* **71**, 3051 (1949).

3. Beck, W., Hieber, W., and Tengler, H., *Chem. Ber.* **94**, 862 (1961).

4. Blyholder, G., and Goodsel, A. J., *J. Catal.* **23**, 374 (1971).

5. Eischens, R. P., and Pliskin, W. A., *in* "Advances in Catalysis" (D. D. Eley, W. G. Frankenburg, V. E. Komarewsky, and P. B. Weisz, Eds.), Vol. 10, p. 1. Academic Press, New York, 1958.

6. Blyholder, G., *J. Chem. Phys.* **44**, 3134 (1966).

7. Blyholder, G., *J. Phys. Chem.* **68**, 2772 (1964).

8. Doyen, G., and Ertl, G., *Surface Sci.* **43**, 197 (1974).

9. Blyholder, G., *J. Vac. Sci. Technol.* **11**, 865 (1974).

10. Peri, J. B., *Discuss. Faraday Soc.* **41**, 121 (1966).

11. Morrow, B. A., and Sheppard, N., *Proc. Roy. Soc. Ser. A* **311**, 391 (1969).

12. Morrow, B. A., and Sheppard, N., *Proc. Roy. Soc. Ser. A* **311**, 414 (1969).

13. Erkelens, J., and Liefkens, T. J., *J. Catal.* **8**, **8**, 36 (1967).

14. Blyholder, G., and Wyatt, W. V., *J. Phys. Chem.* **79**, 618 (1974).

15. Little, L. H., "Infrared Spectra of Adsorbed Molecules." Academic Press, New York, 1966.

16. Blyholder, G., and Neff, L. D., *J. Phys. Chem.* **66**, 1464 (1962).

17. Blyholder, G., *J. Chem. Phys.* **36**, 2036 (1962).

18. Bellamy, L. J., "The Infrared Spectra of Complex Molecules," 2nd ed. Methuen, London, 1958.

19. Fox, J. J., and Martin, A. E., *Proc. Roy. Soc. Ser. A* **167**, 257 (1938); **175**, 208 (1940).

20. Lehmann, W. J., Wilson, C. O., Jr., and Shapior, I., *J. Chem. Phys.* **31**, 1075 (1959).

21. Griffiths, J. E., *J. Chem. Phys.* **38**, 2881 (1963).

22. Bellamy, L. J., "Advances in Infrared Group Frequencies." Methuen, London, 1968.

23. Nakamoto, K., "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, 1963.

24. Ito, K., and Bernstein, H. J., *Canad. J. Chem.* **34**, 170 (1956).

25. Wilmhurst, J. K., *J. Chem. Phys.* **23**, 2463 (1955).

26. Pouchert, C. J., "Aldrich Library of Infrared Spectra," Aldrich Chemical Co. spectrum no. 255B, 1970.

27. Spinner, E., *J. Chem. Soc.* **1964**, 4217.

28. Flett, M. St. C., *Spectrochim. Acta* **18**, 1537 (1962).

29. Sheppard, N., and Ward, J. W., *J. Catal.* **15**, 50 (1969).

30. Morrow, B. A., *Canad. J. Chem.* **48**, 2192 (1970).

31. Ref. (*26*), spectrum no. 1086A.

32. Heck, R. F., and Breslow, D. S., *J. Amer. Chem. Soc.* **83**, 1097 (1961).

33. Paulik, F. E., *Catal. Rev.* **6**, 49 (1972).

34. Blyholder, G., and Neff, L. D., *J. Phys. Chem.* **70**, 1738 (1966).

35. Blyholder, G., and Neff, L. D., *J. Phys. Chem.* **73**, 3494 (1969).

36. Blyholder, G., and Wyatt, W. V., *J. Phys. Chem.* **70**, 1745 (1966).

37. Blyholder, G., and Neff, L. D., *J. Phys. Chem.* **70**, 893 (1966).

38. Blyholder, G., and Neff, L. D., *J. Phys. Chem.* **66**, 1664 (1966).