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FT-IR Study of the Adsorption and Transformation of Formaldehyde on Oxide Surfaces

Guido Busca,[†] Jean Lamotte,[‡] Jean-Claude Lavalley,[‡] and Vincenzo Lorenzelli*[†]

Contribution from the Istituto di Chimica, Facoltà di Ingegneria, Università di Genova, Fiera del Mare, Pad. D, 16129 Genova, Italy, and Laboratoire de Spectrochimie, U.A. 04 414, I.S.M.Ra., Université de Caen, 14032 Caen Cedex, France. *Received December 30, 1986*

Abstract: The adsorption of formaldehyde on different oxides (silica, pure and fluorided alumina, magnesia, titania, thoria, zirconia, and iron oxide) has been studied by FT-IR spectroscopy in the temperature range 170–570 K. The following adsorbed species have been identified and characterized spectroscopically: (i) physisorbed HCHO, (ii) coordinated HCHO, (iii) dioxymethylene, (iv) polyoxymethylene, (v) formate ions, and (vi) methoxy groups. On silica at 170 K formaldehyde physisorbs on surface OH groups and, by warming, polymerizes producing linear polyoxymethylene. On ionic oxides at about 250 K dioxymethylene is always observed, generally together with variable amounts of the linear polymer that has been "isolated" on magnesia at 170 K. Heating up to or above room temperature results in the disproportionation of dioxymethylene into formate and methoxide groups, probably via a Cannizzaro-type mechanism. Such a route probably parallels an oxidative route, involving direct oxidation of dioxymethylene into formates, as observed on iron oxide.

The knowledge of the perturbations and transformations of the C_1 molecules on solid surfaces is necessary for the understanding of the mechanisms of some heterogeneously catalyzed reactions of relevant industrial interest such as CO hydrogenations and methanol conversions.

Formaldehyde is either the product[1] or an intermediate in methanol oxidation[2] and may also be utilized to produce methyl formate via heterogeneously catalyzed Tischenko disproportionation.[3] Moreover, its adsorbed forms are thought to be key intermediates in methanol dehydrogenation[4] and synthesis[5] as well as, possibly, in higher alcohol[6] and Fischer–Tropsch syntheses.[7]

Although several spectroscopic papers have been published recently concerning the adsorption of formaldehyde on oxide surfaces,[8-13] showing almost in all cases complex transformations, the only well characterized adsorbed species besides formate ions is dioxymethylene, whose identifications has been reported by us in a preliminary report.[14]

The present paper summarizes the results of a more complete spectroscopic study of the adsorption and transformation of formaldehyde on oxide surfaces (silica, magnesia, titania, zirconia, thoria, pure and fluorided alumina, iron oxide) with the aim to have a picture as complete as possible of the chemistry and behavior of formaldehyde on oxidic catalysts.

Experimental Section

Some data concerning the characterization and origin of the oxide samples used in the present work are summarized in Table I. The powders were pressed into self-supporting discs of appropriate thicknesses and activated by calcination and evacuation generally at 873 K (723 K in the cases of titania, zirconia, and haematite) into the IR cells. The IR spectra were recorded by Nicolet MXI Fourier transform spectrometers by using variable-temperature quartz cells. Formaldehyde was obtained by evaporation in vacuo of solid paraformaldehyde (Carlo Erba, Milano). This procedure, also because of the very small amount of the powder handled, avoids any possible hazards connected to exposure to the irritating gas HCHO.

Results and Discussion

(1) Spectroscopic Characterization of Some Adsorbed Forms.

(a) Formate Ions. The most evident species arising from the adsorption of HCHO on ionic oxides at room temperature are formate ions.[8-14] The spectroscopic features of such species, characterized mainly by a very strong absorption at 1600–1550 cm^{-1} ($\nu_{(as)CO_2^-}$) and another, usually split or multiple and slightly weaker at 1410–1350 cm^{-1} (δ_{CH} and $\nu_{(s)CO_2^-}$), have been discussed and summarized in previous studies.[15,16] It is, however, of interest to remark that in the ν_{CH} frequency region, that is very useful to identify the adsorbed species, the spectra of formate ions are complex, due to the Fermi resonances between the ν_{CH} fundamental and combinations or overtones of the bands cited above (Table II).[17] Both frequencies and relative intensities vary sig-

Table I. Materials Used

oxide	origin	surface area	structure
SiO_2	Degussa Aerosil 130	133	amorphous
Al_2O_3	Degussa C	96	δ, γ
F/Al_2O_3	impregnation NH_4F	96	δ, γ
MgO	Carlo Erba	31	
TiO_2	Degussa P 25	53	anatase 90%
ZrO_2	ex-isopropilate	85	monoclinic
ThO_2	Rhone–Poulenc	120	
Fe_2O_3	ex-goethite	40	haematite

Table II. Observed Wavenumbers (cm^{-1}) of Adsorbed Formate Ions

ass.	Al_2O_3	ThO_2	ZrO_2	TiO_2	MgO	Fe_2O_3
$\nu_{(a)CO_2^-} + \delta_{CH}$	2970	2950	2965	2970 2950	2930	2960
ν_{CH}	2905	2850	2865	2885 2880	2860 2810	2880
$\nu_{(s)CO_2^-} + \delta_{CH}$	2750	2740	2755 2740	2730	2770 2735	2730
$\nu_{(a)CO_2^-}$	1595	1580 1565	1570	1575 1560	1630 1605	1565
δ_{CH}	1395	1375	1390	1390 1380	1395 1383	1378
$\nu_{(s)CO_2^-}$	1380	1365	1375	1372 1360	1370 1340	1350

[†] Università di Genova.

[‡] Université de Caen.

(1) Le Page, J. F. *Catalyse de Contact*; Technip: Paris, 1978; p 385.

(2) Forzatti, P.; Tronconi, E.; Busca, G.; Tittarelli, P. workshop on *New Developments in Selective Oxidation*; Louvain-la-neuve, 1986; *Catalysis Today* **1987**, *1*, 209.

(3) Ai, M. *J. Catal.* **1983**, *83*, 141.

(4) Cant, N. W.; Tonner, S. P.; Trimm, D. L.; Wainwright, M. S. *J. Catal.* **1985**, *91*, 197.

(5) Klier, K. *Adv. Catal.* **1982** *31*, 243.

(6) Mazanec, T. *J. Catal.* **1986**, *98*, 115.

(7) Biloen, P.; Sachtler, W. M. H. *Adv. Catal.* **1981**, *30*, 165.

(8) Busca, G.; Lorenzelli, V. *J. Catal.* **1980**, *66*, 155.

(9) Yates, J. T.; Cavanagh, R. R. *J. Catal.* **1982**, *74*, 97.

(10) Groff, R. P.; Manogue, W. H. *J. Catal.* **1983**, *79*, 462.

(11) Wang, G. W.; Hattori, H. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 1039.

(12) He, M. Y.; Ekerdt, J. G. *J. Catal.* **1984**, *90*, 17.

(13) Edwards, J. F.; Schrader, G. L. *J. Phys. Chem.* **1985**, *89*, 782.

(14) Lavalley, J. C.; Lamotte, J.; Busca, G.; Lorenzelli, V. *J. Chem., Soc. Chem. Commun.* **1985**, 1006.

(15) Trillo, J. M.; Munuera, G.; Criado, J. M. *Catal. Rev.* **1972**, *7*, 51.

(16) Busca, G.; Lorenzelli, V. *Mater. Chem.* **1982**, *7*, 89.

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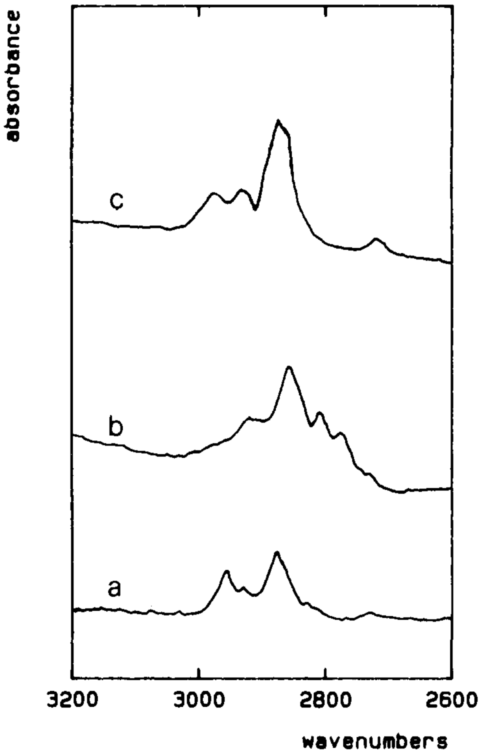

Figure 1. FT-IR spectra (ν_{CH} region) of formate ions adsorbed on iron oxide (a), magnesium oxide (b), and zirconium oxide (c).

Table III. Observed Wavenumbers (cm^{-1}) of Formaldehyde Molecular Species

not.	ass.	gas[a]	O_2 matrix[b]	HBr compl[c]	on SiO_2 180 K	on Al_2O_3 170 K
$2\nu_2$		3471.7	3460.3		3430	3430
$2\nu_3$		2999.5				
$\nu_2 + \nu_6$		3000.1	3001.6		2995	2988
ν_5	$\nu_{(as)CH_2}$	2843.3	2873.6	2886.3	2894	2885
ν_1	$\nu_{(s)CH_2}$	2782.5	2810.1	2819.4	2830	2818
$\nu_3 + \nu_6$		2719.2	2728.4		2732	2725
ν_2	ν_{CO}	1746.1	1740.0	1727.9	1725, 1717	1718
ν_3	δ_{CH_2}	1500.1	1505.3	1495.7	1501	1498, 1485
ν_6	w_{CH_2}	1249.3	1250.2	1247.2		1252
ν_4	r_{CH_2}	1167.1	1171.3	1172.9		

[a] References 19 and 20. [b] Reference 21. [c] Reference 22.

nificantly on different surfaces. This is due to the shift of the ν_{CH} fundamental as a function of the ionicity of the formate group and of the O–C–O angle[18] as well as to the shift of the fundamentals involved in the cited combinations. As an example, the spectra in this region of the formate ions on different surfaces are compared in Figure 1. It may also be remarked that the frequencies of formate ions vary slightly if produced by formic acid adsorption or by formaldehyde or methanol oxidation and shift slightly upon heat treatments.

Besides such formate ions, other species have been sometimes noticed after adsorption at room or lower temperature,[8,9,12] although their identification was almost speculative. To isolate some rather unstable species we have carried out a study of the adsorption at low temperature (down to 170 K).

(b) Adsorption on Silica and Alumina at 170–180 K. Physiadsorbed Formaldehyde. The IR spectrum of HCHO adsorbed at 170 K on silica pretreated at 870 K is reported in Figure 2b. The bands, although showing some relevant perturbations, correspond to those of the free molecule (Table III). The simultaneous perturbation of the free surface OH groups of silica, whose ν_{OH} shifts from 3745 to 3535 cm^{-1}, indicates that they act as adsorption sites. Correspondingly the moderate shift down of the $\nu_{C=O}$ frequencey indicates that, as expected, hydrogen bonding involves the oxygen lone pairs of HCHO, as usual for carbonyl compounds.[23] It is remarkable that, as in the case of acetone adsorbed on silica,[23] the ν_{CO} band of the adsorbed species is split, probably due to the presence of two adsorbed forms differently bonded to one or two nearest surface silanol groups, still present in surfaces treated at moderate temperature under vacuum.[24]

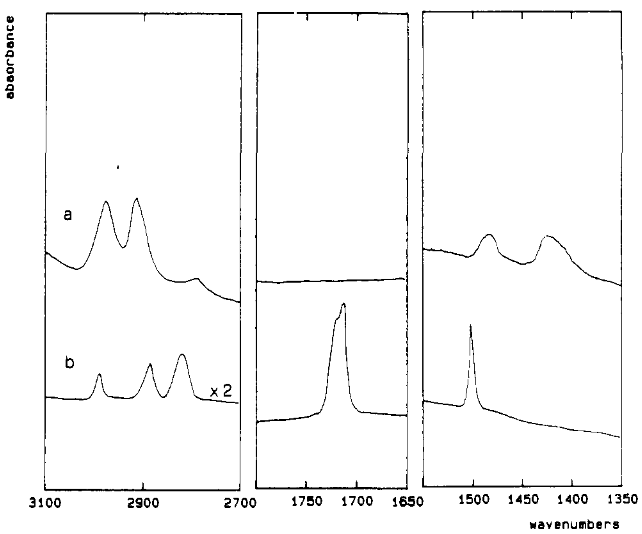

Figure 2. FT-IR spectra of the adsorbed species arising from contact of silica with HCHO gas at 300 K (a) and 170 K (b).

Three rather intense bands are observable in the ν_{CH} region. Both the lower frequency ones, assigned to the asymmetric and symmetric CH_2 stretchings, respectively, are significantly shifted up with respect to the gas-phase values (Table III), as observed in other hydrogen-bonded species as the complexes with hydrogen halogenides.[22,25] The overall IR spectrum is similar to that of matrix-isolated weakly interacting HCHO species and confirms that the low-temperature adsorption on silica represents an alternative technique with respect to that of the isolation in cryogenic matrices to detect weak hydrogen bondings.[26]

By warming up to room temperature the spectrum of HCHO adsorbed on silica completely changes; the sharp ν_{CO} and δ_{CH_2} bands both completely disappear, while in the ν_{CH} region two intense bands are now observed at 2980 and 2915 cm^{-1}, with a weaker absorption near 2805 cm^{-1} (Figure 2a). Very weak bands are also observed in these conditions near 1480, 1425, and 1385 cm^{-1}. A transformation certainly occurred upon warming, possibly polymerization, as will be discussed in the paragraph 1c.

The adsorption of small amounts of HCHO on alumina at 170 K (Figure 3) also produces a species identified as physiadsorbed on surface OH's (Table III). The ν_{OH} bands are accordingly largely perturbed. By increasing the adsorbed amount of formaldehyde ν_{CH} bands at 2980 and 2910 cm^{-1} become predominant showing that also in this case polymerization occurred. In this case the spectra in the lower frequency region, showing very intense absorptions between 1200 and 1000 cm^{-}1 (see also below, Figure 7), indicate that some different species are adsorbed simultaneously, whose nature will be discussed below. In any case we remark that the ν_{CH} spectrum in these conditions closely resembles

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(17) Spinner, E. *Spectrochim. Acta* **1975**, *31A*, 1545.

(18) Shapley, J. R.; StGeorge, G. M.; Churchill, M. R.; Hollander, T. J. *Inorg. Chem.* **1982**, *21*, 3295.

(19) Khoskhoo, H.; Nixon, E. R. *Spectrochim. Acta* **1973**, *29A*, 603.

(20) Brown, L. R.; Hunt, R. H.; Pine, A. S. *J. Mol. Spectrosc.* **1979**, *75*, 406.

(21) Tso, J. L.; Lee, E. K. C. *J. Phys. Chem.* **1984**, *88*, 5475.

(22) Nelander, B. *J. Mol. Struct.* **1980**, *69*, 59.

(23) Bertoluzza, A.; Bonino, G. B.; Fabbri, G.; Lorenzelli, V. *J. Chim. Phys.* **1966**, *63*, 395.

(24) Ghiotti, G.; Garrone, E.; Morterra, C.; Boccuzzi, F. *J. Phys. Chem.* **1979**, *83*, 2863.

(25) Bach, S. B. H.; Ault, B. S. *J. Phys. Chem.* **1984**, *88*, 3600.

(26) Busca, G.; Ramis, G.; Lorenzelli, V.; Janin, A.; Lavalley, J. C. *Spectrochim. Acta*, **1987**, *63A*, 489.

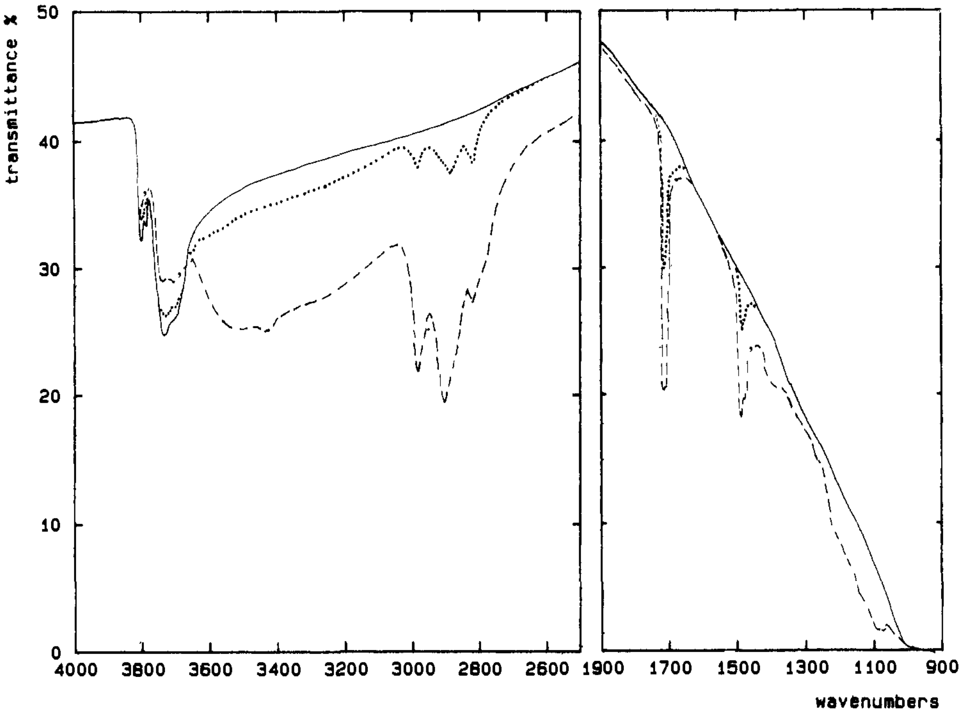

Figure 3. FT-IR spectra of activated alumina (full line) and after adsorption of increasing amounts of formaldehyde at 170 K (point and broken lines).

Table IV. Observed Wavenumbers (cm^{-1}) of Polyoxymethylene

		HCHO on		
ass.	hexagonal POM[a]	MgO 230 K	SiO_2 rt	Al_2O_3 170 K
ν_{CH_2}	2984	2980	2980	2980
	2920	2918	2915	2910
δ_{CH_2}	1471	1485	1480	
w_{CH_2}	1434	1430	1425	
	1384	1395	1385	
t_{CH_2}	1290	1325, 1290		
	1238	1235		1230, 1210
r_{CH_2}	1098	1115, 1105		1110
ν_{CO}	936	940		
	897	910		

[a] Reference 27.

that reported by Yates and Cavanagh in similar conditions,[9] although the predominant bands were assigned to HCHO adsorbed as such.

(c) Adsorption on Magnesia at 170 K. Polyoxymethylene. The spectrum of formaldehyde adsorbed on magnesia at 170 K (Figure 4) is characterized by very intense bands at 1238, 1105, and 935–908 cm^{-1}, assignable to ν_{C-O} frequencies. In the ν_{CH} region rather strong bands at 2980 and 2918 cm^{-1} are observed, with a broad shoulder near 2790 cm^{-1}. Weaker bands are also observable in the 1500–1300-cm^{-1} region (Table IV). The spectrum in the region above 1300 cm^{-1} is very similar to that observed on silica at room temperature. The overall spectrum is very similar to that reported for the hexagonal polyoxymethylene,[27] allowing then its assignment to a similar adsorbed species. It is worth noticing that while on silica the OH band of surface hydroxyls is strongly perturbed by formaldehyde adsorption and polymerization (ν_{OH} broadened and shifted from 3745 to 3450 cm^{-1}), on magnesia it is almost unperturbed (3750 cm^{-1}). Polymerization then, that on silica at room temperature is certainly catalyzed by the rather acidic surface OH groups, on magnesia is very likely due to the basic anionic sites. Accordingly, it is known that formaldehyde polymerization may occur through both a cationic and an anionic mechanism.[28] On the other hand, it is well known that magnesia is a useful catalyst for the polymerization of ethylene oxide to produce polyoxyethylene,[29] probably via a similar base-catalyzed mechanism.

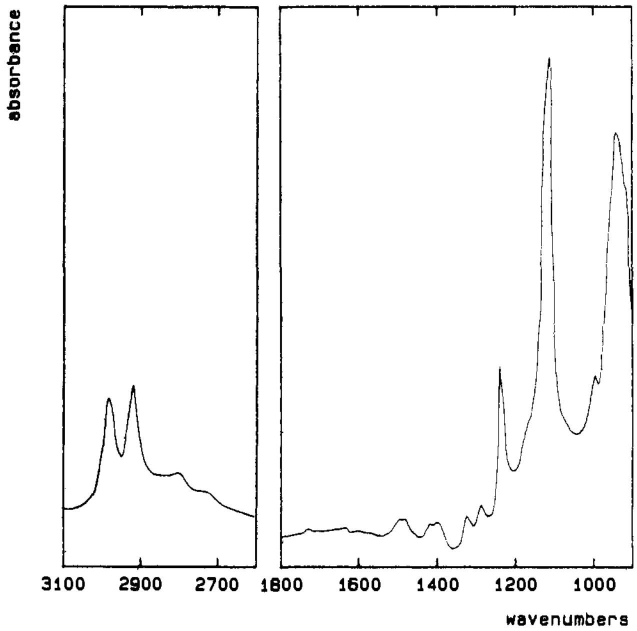

Figure 4. FT-IR spectrum of the adsorbed species arising from contact of magnesia with formaldehyde gas at 170 K.

The formation of the linear polymer has already been proposed concerning a species characterized by ν_{CH}'s at 2950 and 2920 cm^{-1} arising from the room temperature adsorption of HCHO on haematite,[8] although this assignment has been later criticized.[12] The spectrum of the linear polymer in the ν_{CH} region is also very similar to that observed on alumina, both by us and by Yates and Cavanagh,[9] at 280–150 K. The presence in our conditions of strong bands in the region 1300–1000 cm^{-1} (Figure 3) confirms that polymerization of formaldehyde occurs also on alumina, although other species (dioxymethylene, see section 1d) are also present. As we have confirmed, formaldehyde may polymerize, although to a different extent, on several oxide surfaces, as pre-

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(27) Zamboni, V.; Zerbi, A. *J. Polym. Sci.* **1963**, *C7*, 153.

(28) *Polyaldehydes*; Vogl, O., Ed.; Arnold: London, 1967.

(29) Eastham, A. M.; *Fortschr. Hochpolym.* **1960**, 18.

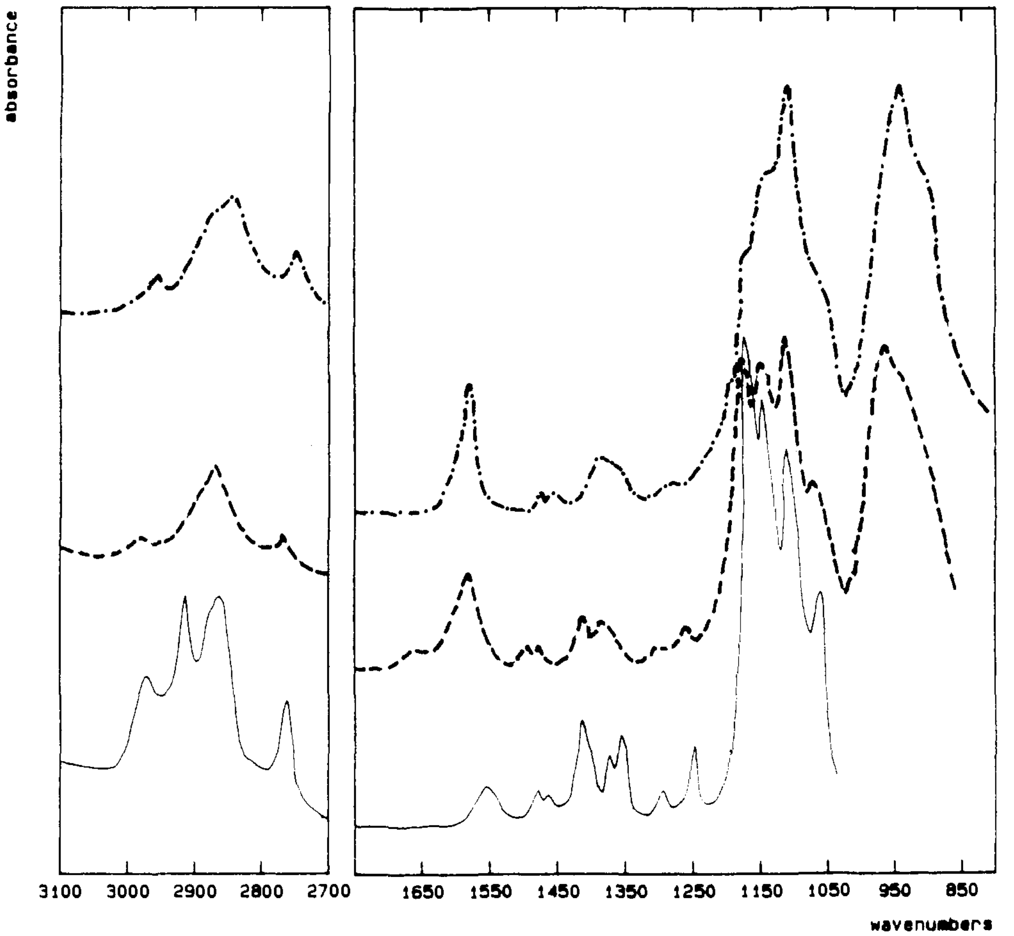

Figure 5. FT-IR spectra of species arising from formaldehyde adsorption on titania (full line), zirconia (broken line), and thoria (dashed line) at 250 K.

viously reported for germania,[30] even at very low temperature.

It may be noticed that in our experiments we never have observed the formation of the cyclic trimer *s*-trioxane, that may be identified spectroscopically, among others, by a ν_{CH} band above 3000 cm^{-1}.[31]

(d) Adsorption on Zirconia, Thoria, and Titania at 200–250 K. Dioxymethylene. The spectra of HCHO adsorbed at 240 K on zirconia and thoria and at 270 K on titania are compared in Figure 5. In all cases together with weak bands near 1550 and 1390–1360 cm^{-1}, due to formate ions, very strong bands are observed in the 1200–1000-cm^{-1} region, presenting at least four maxima, while a broad band is also observed between 1000 and 800 cm^{-1} on both zirconia and thoria, whose background limit is sufficiently low to allow the inspection of this region. At higher frequencies weaker bands are also observed in similar positions on all three surfaces (Table V), the most intense being placed at about 1410 cm^{-1}. Also in the ν_{CH} region the spectra show very similar features, sharp bands being observed at near 2870–2840 and at 2765–2750 cm^{-1}, while a weaker and broader one is also observed at near 2950 cm^{-1}. Only on titania a further sharp band may be observed at 2910 cm^{-1}, probably due to small amounts of the linear polymer cited above. The bands we observe on such surfaces are compared in Table V with those of the compounds dimethoxymethane-d_6 and dioxolane-d_4. The close similarity of the spectra confirms our previous identification of the corresponding surface species as a dioxymethylene group,[14] although the multiplicity of the ν_{C-O} bands may suggest the presence of different conformers. Experiments of HCH^{16}O adsorption on ^{18}O-exchanged thoria surfaces have shown that the intermediate dioxymethylene species is almost symmetrical, since the same amount of CH$_3{}^{16}$OH and CH^{18}OH was formed via their disproportionation,[14] as discussed below. The formation of dioxymethylene is certainly correlated with the reaction of the HCHO molecule with a cation–anion couple and is justified by the very high electrophilicity of the carbonyl carbon, possibly further enhanced by coordination on the cationic site. We may mention that the existence of a similar species is reported in the literature in the complex (CH$_2$O$_2$)Mo$_4$O$_{12}$(OH)$^{3-}$, characterized by some strong absorptions in the region 1200–1000 cm^{-1}, whose structure has been determined by diffraction methods.[35]

Table V. Observed Wavenumbers (cm^{-1}) of Dioxymethylene Species

ass.	H$_2$C-(OCD$_3$)$_2$[a]	dioxolane-d_4[b]	CH$_2$O on TiO$_2$	CH$_2$O on ZrO$_2$	CH$_2$O on ThO$_2$
$\nu_{(as)CH_2}$	2945	2955			
			2950	2970	2960
$2\delta_{CH_2}$	2932	3013			
$\nu_{(s)CH_2}$	2882	2845	2868	2870	2840
$2w_{CH_2}$	2770	2738	2763	2765	2750
δ_{CH_2}	1473	1510	1482, 1464	1490, 1470	1495
w_{CH_2}	1401	1383	1418–1408	1410	1405
t_{CH_2}	1302		1300	1315	1280
	1186		1251	1255	
	1138		1172, 1156	1180, 1157	1180, 1150
r_{CH_2}	1114		1113	1117	1112
ν_{C-O}	1086		1070	1070	1070
				965	948
	858			890	920

[a] References 32 and 33. [b] Reference 34.

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(30) McManus, J. C.; Matsushita, K. I.; Low, M. S. D. *Can. J. Chem.* **1969**, *47* 1077.

(31) Kobayashi, M.; Iwamoto, R.; Tadokoro, K. *J. Chem. Phys.* **1966**, *44*, 922.

(32) Nukada, K. *Spectrochim. Acta* **1983**, *18*, 745.

(33) Saur, O.; Travert, J.; Lavalley, J. C.; Sheppard, N. *Spectrochim. Acta* **1973**, *29A*, 243.

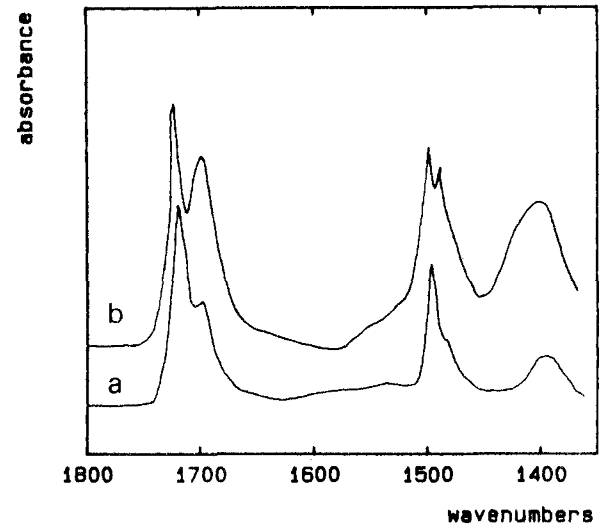

Figure 6. FT-IR spectra (1800–1350 cm^{-1}) of species arising from formaldehyde adsorption on haematite at 175 K (a) and 205 K (b). The band near 1400 cm^{-1} is due to dioxymethylene.

(e) Coordinated Formaldehyde. Working at low temperature, we have attempted to isolate the molecule simply chemisorbed on Lewis acid sites. However, as already reported in section 1b, working at temperatures as low as 170 K, even on surfaces having a predominant Lewis acidic character, as alumina, adsorbed species characterized by ν_{CO} near 1720 cm^{-1} may be observed that are certainly bonded to surface hydroxy groups. The corresponding ν_{OH} bands are in fact simultaneously perturbed. This would indicate that hydrogen bonding is kinetically preferred in such conditions with respect to coordination. By slow warming, the linear polymer and/or the dioxymethylene species are rapidly formed on all surfaces we have investigated. However, in several cases (as on titania and iron oxide) a second ν_{CO} band is intermediately observed, near 1700–1680 cm^{-1}, due to a more perturbed molecular form of HCHO, probably coordinated on Lewis acid sites. Such a species is associated with a δ_{CH_2} vibration at slightly lower frequency (about 1480 cm^{-1}) than that characterizing the physisorbed species (Figure 6 for iron oxide). Also on alumina, at intermediate temperatures (near 200 K) a new species becomes detectable, characterized by a strong band at 1680 and a much weaker one at 1490 cm^{-1} (Figure 7a). Such species is also evident on the stronger Lewis acid fluoridated alumina (Figure 7b), although also on these surfaces it is present together with other compounds (dioxymethyene, polyoxymethylene). Assignment of these three bands to coordinated HCHO is likely (1680 cm^{-1} $\nu_{C=O}$; 1490 cm^{-1} δ_{CH_2}). In any case, we were not able to identify without ambiguity the ν_{CH} absorptions of such species, due to the superposition with those of other adsorbed species, although we may suppose they are not so different from those of physysorbed HCHO. In all cases coordinated formaldehyde is very unstable, being detectable only at low temperature.

(2) Transformation upon Warming. The thermal transformation of adsorbed formaldehyde on the covalent oxide silica has been discussed in section 1c. As for all ionic oxides, the thermal behavior shows a strong parallelism both on surfaces having a predominant basic character, as magnesia, zirconia, thoria, and on surfaces usually considered as mainly acidic, as alumina, titania, and iron oxide. At moderately low temperatures (230–270 K) the spectra indicate that dioxymethylene may be predominant, as reported in Figure 5 for zirconia and thoria, or mixed with polyoxymethylene, as shown in Figure 5 for titania (see also Figures 2 and 7 for alumina). On magnesia, where at 170 K the polymer appears largely to be isolated (the bands of dioxymethylene cannot be observed), the transformation of the linear polymer into dioxymethylene is progressively detected in the same range of temperatures (Figure 8). On all cited surfaces, by further

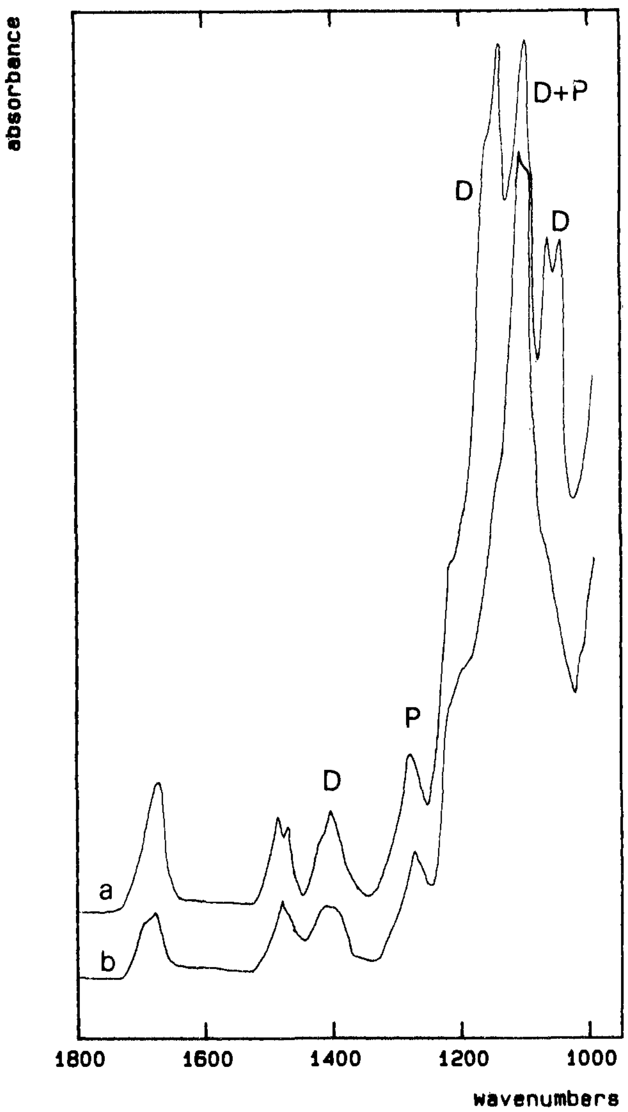

Figure 7. FT-IR spectra (1800–1350 cm^{-1}) of species arising from formaldehyde adsorption on alumina (a) and fluoridated alumina (b) at 200 K. The bands noticed with P and D are attributed to polyoxymethylene and dioxymethylene, respectively.

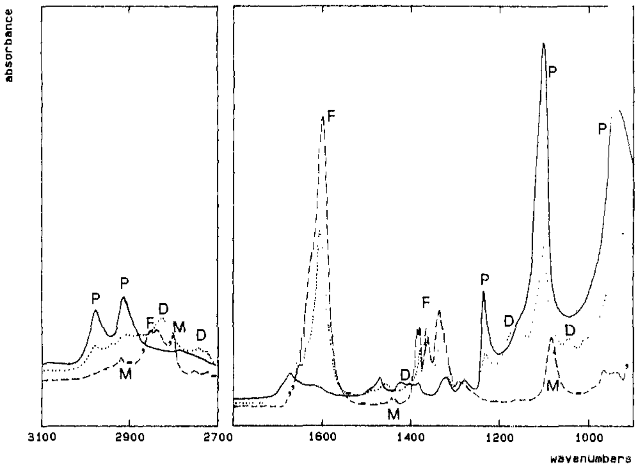

Figure 8. FT-IR spectra of species arising from formaldehyde adsorption on magnesia upon different thermal treatments in vacuo: 260 K (full line), 300 K (point line) and 520 K (broken line). The bands noticed with P, D, F, and M are due to polyoxymethylene, dioxymethylene, formate ions, and methoxy groups, respectively.

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(34) Saur, O.; Janin, A.; Lavalley, J. C.; Sheppard, N. *C. R. Acad. Sci., Ser. B* **1973**, *276*, 725.

(35) Day, V. W.; Friedrich, M. F.; Klemperer, W. G.; Liu, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 491.

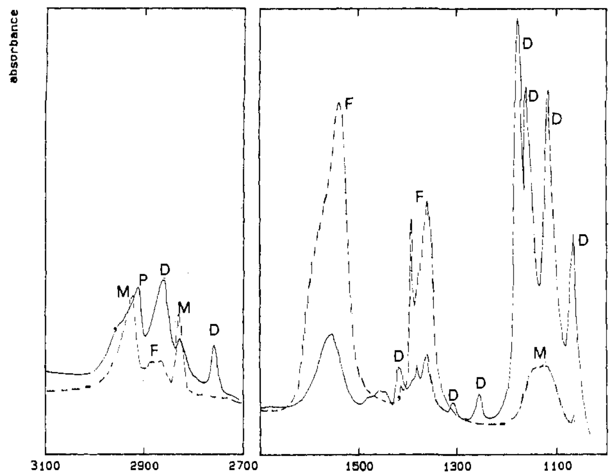
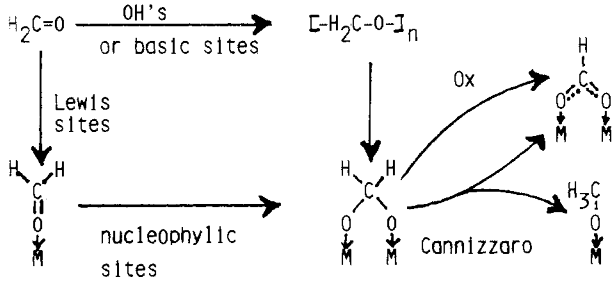


Figure 9. FT-IR spectra of species arising from formaldehyde adsorbed on titania upon different thermal treatments in vacuo: 300 K (full line) and 420 K (broken line). For the band notation, see Figure 8.

Scheme I



warming up to 270–300 K the very intense bands due to formate ions begin to develop. However, in almost all cases, such bands appear together with sharp absorptions in the region 2950–2900 and 2850–2800 cm^{-1}, very weak split bands near 1450 cm^{-1} and relatively intense bands in the 1000–1100-cm^{-1} regions; all these are assignable to methoxy groups (noted with M in Figures 8 and 9). This assignment has been confirmed on all cited surfaces by comparison with the spectra of adsorbed species arising from methanol adsorption.[8,36,38]

The formation of methoxy and formate groups, at the expense of the dioxymethylene intermediate, suggests that a Cannizzaro-type disproportionation occurs. The formation of gas-phase $CH_3{}^{18}OH$ together with $CH_3{}^{16}OH$ after adsorption of $HCH^{16}O$ adsorption on ^{18}O-exchanged thoria surface[14] confirms such a mechanism, showing also the role of surface oxygen in such a disproportionation reaction. In the cases of magnesia (Figure 8), titania (Figure 9), zirconia, thoria, and alumina formate and methoxy groups, these are the only species still present on the surface after heating up to about 370 K. On iron oxide, instead, after such a treatment we have no evidence of the presence of methoxy groups. However, we may note that on such a surface the methoxy groups, formed by methanol adsorption, are themselves oxidized to formates at very mild temperatures.[8] However, we cannot exclude that a further possible evolution of dioxymethylene on very strongly oxidizing surfaces is their direct oxidation to formates. We have some evidence of this on vanadium–titanium oxide methanol oxidation catalysts.[39]

Conclusions

The results presented and discussed above indicate that the adsorption and transformation of formaldehyde follows an almost generalized pathway on all ionic oxide surfaces we have investigated. Such a pathway may be schematized as follows. Scheme I may be useful to interpret the role of the adsorbed species of formaldehyde both in methanol oxidation reactions and in CO hydrogenations over oxidic surfaces or on catalysts where the oxidic support may play a role.

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Registry No. Formaldehyde, 50-00-0; silica, 7631-86-9; fluoride, 16984-48-8; alumina, 1344-28-1; magnesia, 1309-48-4; titania, 13463-67-7; thoria, 1314-20-1; zirconia, 1314-23-4; iron oxide, 1309-37-1; formate, 71-47-6.

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(36) Busca, G.; Rossi, P. F.; Lorenzelli, V.; Benaissa, M.; Travert, J.; Lavalley, J. C. *J. Phys. Chem.* **1985**, *89*, 5433.

(37) Busca, G.; Forzatti, P.; Lavalley, J. C.; Tronconi, E. In *Catalysis by Acids and Bases*; Imelik, B., et al., Eds.; Elsevier: Amsterdam, 1985; p 14.

(38) Montagne, X.; Lamotte, J.; Lynch, J.; Freund, J.; Lavalley, J. C. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 1617.

(39) Busca, G.; Elmi, A. S.; Forzatti, P. *J. Phys. Chem.*, in press.