Fourier Transform I.R. Evidence of the Formation of Dioxymethylene Species from Formaldehyde Adsorption on Anatase and Thoria

Jean-Claude Lavalley,*[a] Jean Lamotte,[a] Guido Busca,[b] and Vincenzo Lorenzelli[b]

[a] *Laboratoire de Spectrochemie, Groupe 'Structure et Réactivité d'Espèces Adsorbées,' U.A. 414, I.S.M.Ra, Université, 14032, Caen Cedex, France*

[b] *Istituto di Chimica, Facolta di Ingegneria, Fiera del Mare Pad D. Universita di Genovà, 16129 Genova, Italy*

HCHO adsorption on activated thoria produces, at 240 K, a species characterized as dioxymethylene; by heating at room temperature, it leads to formate and methoxy groups: the three species are observed by adsorption of HCHO on anatase at room temperature.

In recent years, much effort has been devoted to the identification of the mechanisms of C_1-molecule conversions catalysed by solid surfaces. These studies have been particularly related to important processes such as CO hydrogenations (Fischer–Tropsch, methanol, and higher alcohols syntheses), methanol conversions, and formaldehyde and methyl formate syntheses.[1]

In such processes, formaldehyde adsorbed species may play a key role. However, even if a number of complexes of formaldehyde with transition metals have been identified and their chemistry described,[1,2] rather few data are available on HCHO chemistry on solid surfaces. Previous studies have shown formate ions to be the predominant adsorbed form on oxides such as Fe_2O_3,[3] Al_2O_3,[4] MgO,[5] TiO_2 (rutile[6]), and

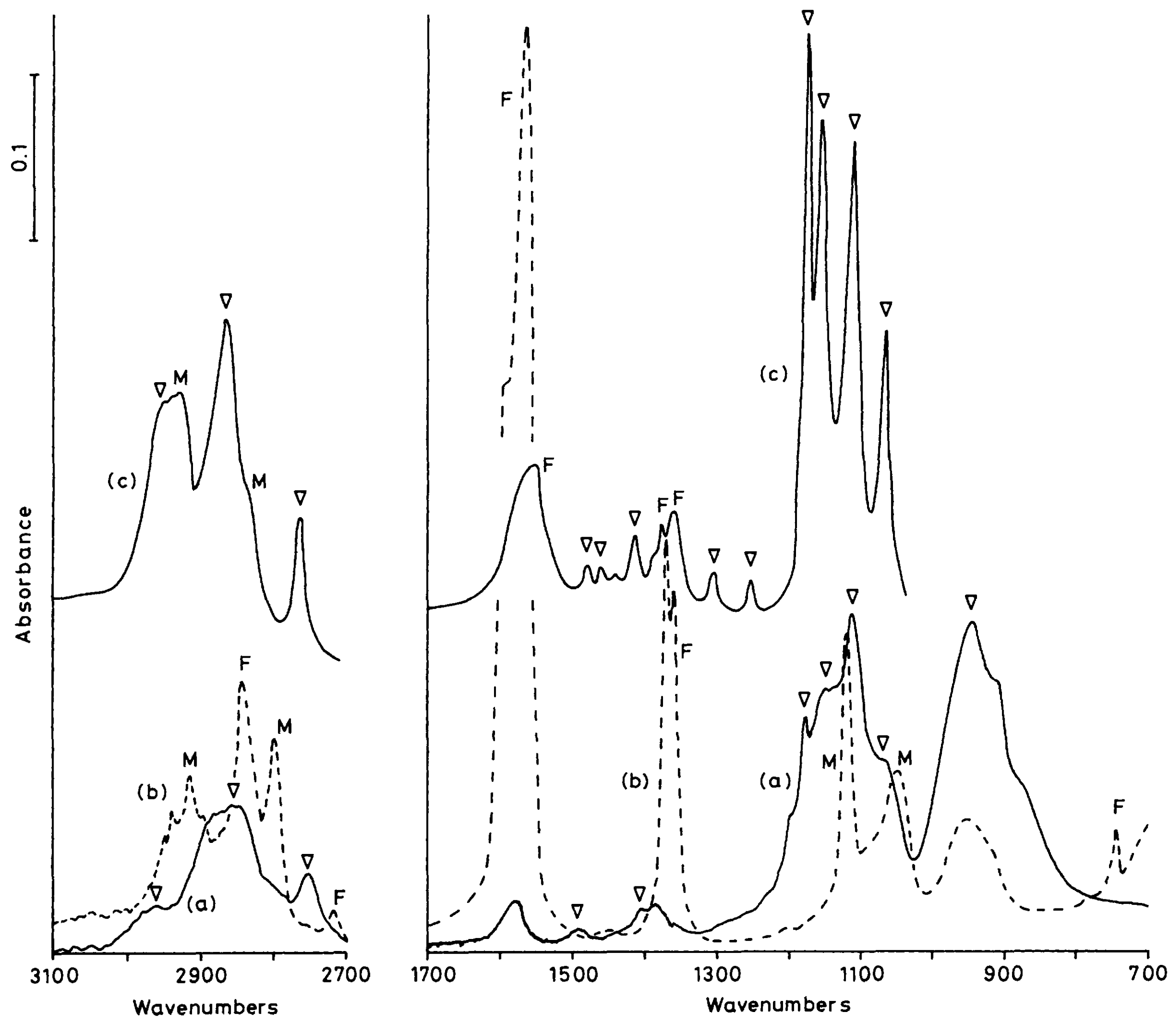


Figure 1. I.r. spectra of species given by HCHO adsorption on thoria at 240 K (a—), and following heating at room temperature (b--), and on anatase at room temperature (c—). The characteristic bands of methoxy (M), formate (F), and dioxymethylene (∇) species are indicated. For convenience, the absorbance scale in the 3100—2700 cm^{-1} range has been slightly expanded. TiO_2 is not transparent below 1000 cm^{-1}.

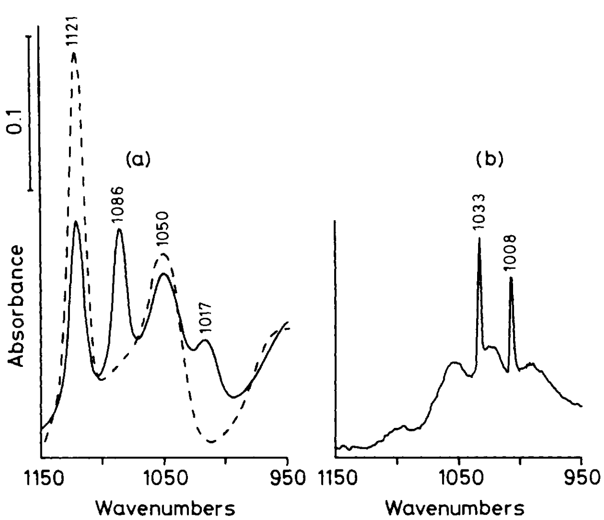


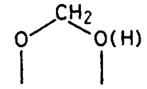
Figure 2. (a) I.r. spectra of ν(CO) methoxy groups formed from HCHO adsorption at room temperature on thoria (– –) and on thoria exchanged with $H_2{}^{18}O$ (——); (b) gas phase spectrum of methanol produced by heat desorption of methoxy groups formed by HCHO adsorption on exchanged thoria.

ZrO_2.[7] Spectroscopic features of molecularly adsorbed formaldehyde[3,4] and of other adsorbed species,[3,7] still poorly identified, have only been observed sometimes. Formyl species have been observed from CO/H_2 coadsorption on ZnO.[8]

We report here, on TiO_2 (anatase) and on ThO_2, some results of a HCHO adsorption study that allow identification of other adsorbed forms of formaldehyde. Anatase (Degussa P 25) and thoria (Rhône–Poulenc) were pressed into discs which were then activated under O_2 and vacuum respectively at 670 and 970 K. The spectra were recorded using Nicolet MX-1 interferometers.

HCHO adsorption at 240 K on thoria leads to a species characterized by two complex and relatively broad bands at 1112 and 945 cm^{-1}. In the ν(CH) frequency range, bands at 2960 (shoulder), 2850 (broad), and 2750 cm^{-1} appear (Figure 1a). By heating at room temperature, all these bands disappear while bands due to formate (2840, 1575, 1375, 1363, and 748 cm^{-1}) and methoxy groups (2920, 2805, 1445, 1121, and 1050 cm^{-1}) are apparent (Figure 1b). HCHO adsorption on TiO_2 anatase at room temperature also gives rise to formate and methoxy groups (Figure 1c) together with bands (2950, 2868, 2763, 1408, 1172, 1156, 1113, and 1070 cm^{-1}) close to those observed on thoria at 240 K.

In order to characterize the formation and the nature of all the species, we have also studied the adsorption at room temperature of HCHO on ThO_2 isotopically exchanged with $H_2{}^{18}O$ at 570 K[9] and finally evacuated at 570 K. It appears, in such a case, that the ν(CO) bands typical of methoxy groups are split (Figure 2a), the two bands at 1121 and 1050 cm^{-1} being due to $CH_3{}^{16}O$ groups, while the others (1086, 1017 cm^{-1}) characterize the $CH_3{}^{18}O$ groups. Accordingly, after heating at 370 K, we observe in the gas phase the formation of $CH_3{}^{16}OH$ and $CH_3{}^{18}OH$ (bands at 1033 and 1008 cm^{-1} respectively) in nearly equivalent amounts (Figure 2b).



(A)

This latter experiment shows that surface oxide ions participate in formaldehyde adsorption. We propose for the first step the formation of a structure such as (A) that transforms later into methoxy and formate groups.

The i.r. spectrum of the first species we observed agrees with such a structure: bands at 960 and 1100 cm^{-1} have been assigned to a similar species in the case of HCHO adsorption on Ag (110) where oxygen was previously atomically adsorbed.[10] Moreover, very similar ν(CH) bands have been observed in dioxymethylene organic compounds such as dioxolane(D_4).[11]

The formation of formate and methoxy groups can be explained by a Cannizzaro type mechanism which is known to take place in basic media. Accordingly, we have observed that thoria surfaces have a strong basic character.[12] In contrast, titania surfaces are generally considered as rather acidic.[13] However, their basicity has not been studied in detail yet and it has been reported[14] that TiO_2 is reactive towards HCHO (Tischenko dimerization) to produce methyl formate. For this reaction, both acidic and basic sites have been considered to be necessary.

It is possible that the Cannizzaro type reaction is quite important in methanol synthesis from CO + H_2 on basic oxides such as ThO_2. The formic species formed may decompose under the reaction conditions, restoring CO and leading finally to only methanol.

Received, 19th March 1985; Com. 364

References

1 G. Henrici-Olivé and S. Olivé, 'The Chemistry of the Catalyzed Hydrogenation of Carbon Monoxide,' Springer Verlag, Berlin, 1984.
2 D. L. Thorn, *J. Mol. Catal.*, 1982, **17**, 279.
3 G. Busca and V. Lorenzelli, *J. Catal.*, 1980, **66**, 155.
4 J. T. Yates and R. R. Cavanagh, *J. Catal.*, 1982, **74**, 97.
5 G. W. Wang and H. Hattori, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 1039.
6 R. P. Groff and W. H. Manogue, *J. Catal.*, 1983, **79**, 462.
7 M. Y. He and J. G. Ekerdt, *J. Catal.*, 1984, **90**, 17.
8 J. Saussey, J. C. Lavalley, J. Lamotte, and T. Rais, *J. Chem. Soc., Chem. Commun.*, 1982, 278; J. C. Lavalley, J. Saussey, and T. Rais, *J. Mol. Catal.*, 1982, **17**, 289.
9 J. C. Lavalley and M. Benaissa, *J. Chem. Soc., Chem. Commun.*, 1984, 908.
10 E. M. Stuve, R. J. Madix, and B. A. Sexton, *Surf. Sci.*, 1982, **119**, 279.
11 O. Saur, A. Janin, J. C. Lavalley, and N. Sheppard, *C.R. Acad. Sci., Ser. B*, 1973, **276**, 725.
12 J. Lamotte, J. C. Lavalley, E. Druet, and E. Freund, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 2219.
13 G. Busca, H. Saussey, O. Saur, J. C. Lavalley, and V. Lorenzelli, *Appl. Catal.*, 1985, **14**, 245.
14 M. Ai, *J. Catal.*, 1983, **83**, 141.