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Infrared Study of the Reaction of Adsorbed Formate Ion with H_2 on Supported Rh Catalysts

Infrared spectroscopy is currently widely used to monitor the catalyst surface during the catalytic hydrogenation of CO, and to identify the species presumed to be of importance in the reaction.

One of the surface species observed in the methanation reaction is the formate ion (*1–3*). While it was earlier assumed that this species is a possible surface intermediate in the methanation reaction, with the growing importance of surface carbon in this hydrocarbon synthesis the role of formate species in the reaction is nowadays almost entirely ignored. The presence of formate in the hydrogenation of CO on Ru/Al_2O_3 catalyst was recently demonstrated by ir spectroscopy (*4*). It was claimed, however, that the formate ion was formed directly on the alumina and that its formation did not require metallic Ru. It was regarded as an inactive reaction product or as a byproduct adsorbed on the alumina support.

The formate ion has also been observed in the low-temperature interaction of H_2 + CO_2 and during the methanation of CO_2 on alumina-supported Rh and Ru (*5–9*). As it was formed at a much lower temperature (313–373 K) than on pure alumina (*10, 11*), it was concluded that its formation is effectively promoted by the metal. This was reflected in the lower activation energy of its formation (*5, 8*).

Although there is no doubt that the metal plays an important role in the formation of formate ion in this reaction, from the results of more detailed measurements with supported Rh it has become evident that the formate ion is most probably located on the support and virtually not at all on the Rh (*8*). The question remains open, however, as to whether the formate ion is *completely* inert, or whether its reaction also contributes to methane formation.

Although the formate ion has been found to be relatively stable at the methanation temperatures of CO_2(443–523 K) *in vacuo* or in a He flow, *in situ* ir spectroscopic measurements have shown that a proportion of it can easily be eliminated by H_2. This prompted us to investigate more closely the reactivity of adsorbed formate ion toward H_2, and the products of this reaction. The present report gives an account of our results obtained with Rh on different supports.

The Rh samples were the same as used in the study of the H_2 + CO_2 interaction (*5, 8*) and in the methanation of CO_2 (*7*). The samples were oxidized and reduced *in situ* at 673 K. Infrared spectra were recorded with a Specord 75 IR double-beam spectrometer (*5*). Two different cells were used. In the high-temperature cell, which was similar to that described in our other paper (*12*), the spectra were taken at the reaction temperature, *in vacuo* or in the gas flow. The products of the surface reaction were analyzed with a Hewlett–Packard gas chromatograph. In a specially designed microcell, spectra were taken at the temperature of the infrared beam (~313 K). The pellet pretreatments and the reaction were carried out in one end of the cell, around which a small furnace was placed. The small volume of the cell (~15 ml) made it possible to flush the gas phase entirely into the gas chromatograph column.

Adsorption of 0.1–2 Torr formic acid on Rh/Al_2O_3 produced strong bands at 1590 and 1380 cm^{-1} and weaker one at 1395 cm^{-1} (*5*). A very weak band at 2915–2926 cm^{-1} was also identified. On elevation of the

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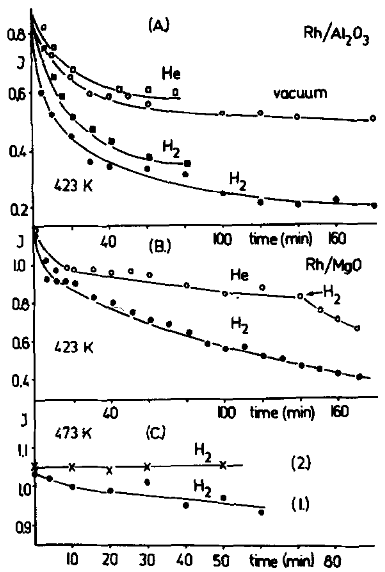

FIG. 1. Changes in the intensities of the formate bands (1590–1600 cm^{-1}) on different catalysts in a He or H$_2$ flow. (A) 1 wt% Rh/Al$_2$O$_3$; (B) 1 wt% Rh/MgO; (C): (1) Al$_2$O$_3$, (2) MgO. $I = \log T_0/T$.

temperature to 423 K, the intensities of the formate bands initially decreased rapidly, but afterward they remained constant (Fig. 1). During decomposition of the formate ion, a weak band appeared at 1443 cm^{-1} in the spectrum; this can be attributed to a surface carbonate species. The surface formate decomposed to CO$_2$ and H$_2$ (~70%) and to CO and H$_2$ (~30%). Methane was found merely in traces (~0.2%).

On admission of H$_2$ into the He flow, or in the presence of pure H$_2$, the intensities of the formate bands decreased much faster and to a greater extent than in a pure He flow or *in vacuo* (Fig. 1). Complete elimination of the formate bands, however, was not attained at this temperature, even in the presence of H$_2$; about 20–30% of the formate proved rather unreactive toward H$_2$. Gas-chromatographic analysis of the gas phase showed that a considerable amount of CH$_4$ was formed in the reaction of surface formate and H$_2$.

Adsorption of formic acid on the alumina support alone produced the same absorption bands as on Rh/Al$_2$O$_3$ (*5*). These bands were stable below 523 K *in vacuo* or in a He flow. In contrast to the findings on the Rh/Al$_2$O$_3$ sample, their intensities hardly changed in the presence of H$_2$ at 298–473 K (Fig. 1).

For quantitative determination of the extent of transformation of surface formate into CH$_4$, further experiments were performed in a micro ir cell. After production of surface formate, the sample was evacuated at 298 K for 10 min and H$_2$ was introduced into the cell at 298 K. The sample was heated quickly to the reaction temperature and kept there for a certain time (5–15 min) before the gas phase was flushed into the analyzing column of the gas chromatograph.

At the beginning of the reaction, weak bands were observed at 2030 and 1770 cm^{-1}. Figure 2 shows the changes in the surface concentration of formate ion during the reaction, and the amount of methane formed. The relation between the amounts of methane formed and of formate reacted is also indicated. The surface concentration of formate ion was calculated on the basis of the correlation between the absorbance of the formate band at 1590 cm^{-1} and the

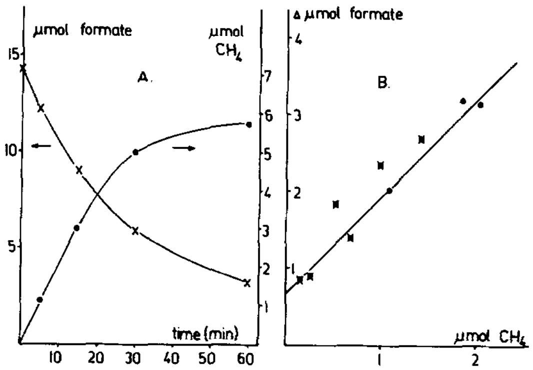

FIG. 2. (A) Changes in the surface concentration of formate ion and the amount of methane formed on Rh/Al$_2$O$_3$ in the presence of H$_2$ at 423 K. The experiments were carried out in the microcell (~15 ml) in the presence of 650 Torr H$_2$. (B) The relation between the amounts of formate reacted and of methane formed in the reaction on Rh/Al$_2$O$_3$ at 423 K. The amount of catalyst disk was 60 mg. ●, ■ represent the results of two experiments.

amount of formate ion on the alumina (*10*). It appears that about 70–75% of the surface formate on Rh/Al_2O_3 reacted in the presence of H_2 in 60 min at 423 K. This corresponds to 11 μmol formate ion. At the same time 5.74 μmol CH_4 was formed. If we take into account the amount of surface formate decomposed under similar conditions in He (~5.5 μmol), and assuming that this self-decomposition occurs unchangingly in the presence of H_2 as well, it is found that in the hydrogen–formate reaction on Rh/Al_2O_3 one formate ion is converted to approximately one CH_4.

When the Rh content of the catalyst was increased to 5 wt%, the rate of the reaction was considerably higher. In this case a strong band at 2030 cm^{-1}, due to adsorbed CO, was identified during the reaction.

The changes in the stability and the reaction of surface formate in the presence of H_2 are well demonstrated by the temperature-programmed reaction (TPR) spectra of formate adsorbed on Rh/Al_2O_3 (Fig. 3). Obviously, the reaction conditions in this case are basically different from those existing under isothermal conditions at 423 K. Thus, the hydrogenation of formate decomposition products (CO and CO_2) can contribute greatly to the methane formation. Nevertheless, the TPR spectra unambiguously show the effect of H_2 on the reactivity of formate ion.

Similar measurements were performed on Rh/MgO. The changes in the intensities of the formate band at 1590–1600 cm^{-1} for Rh/MgO in the absence and in the presence of H_2 are illustrated in Fig. 1. On the action of H_2 the intensities of formate bands rapidly decreased. The conversion to CH_4 in this case, however, was much less than on Rh/Al_2O_3. The ratio of the amounts of CH_4 formed and of formate reacted varied in the range 0.05–0.1. The main product of the reaction was CO. No influence of H_2 on the stability of formate ion on the MgO support was observed at the same temperatures (Fig. 1).

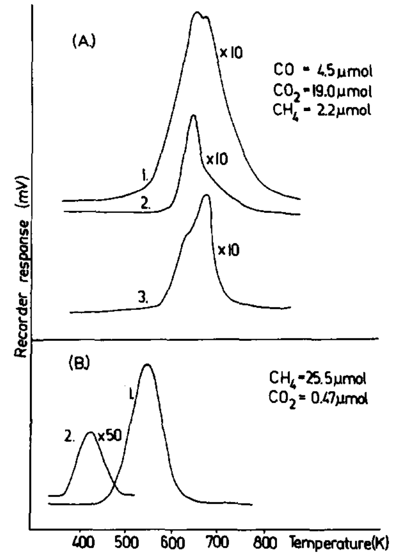

FIG. 3. (A) Product peaks in He flow from TPR of HCOOH (26.1 μmol) adsorbed on Rh/Al_2O_3 at room temperature: (1) CO + CO_2 + CH_4 (with TCD detector); (2) CO (with TCD detector); (3) CH_4 (with FID detector). (B) Product peaks in a H_2 flow from TPR of HCOOH (26.1 μmol) adsorbed on Rh/Al_2O_3 at room temperature. (1) CH_4 (with FID detector); (2) CO_2 (with TCD detector). The flow rate of He (A) and H_2 (B) was 40 ml/min. The heating rate was 40°/min.

The data show that the formate ion, which is formed in the hydrogenation of both CO and CO_2, is not so inactive as was thought: in spite of the fact that it resides on the support rather than on the active metal component, it reacts with H_2 to yield CH_4. As this reaction was not observed in the absence of metal, it indicates that the molecular H_2 does not react directly with the formate group, but that the activation of the H_2 on the Rh is required for the reaction. We presume, that in the first step H_2 dissociates on the metal, and that the activated hydrogen migrates to the formate group on the support, reacting with it to produce CH_4.

Since the hydrogenation of CO on Rh/Al_2O_3 *is negligible under similar conditions, it may be assumed that the methanation of the formate group does not involve the transient formation and hydrogenation of CO.*

We note that the addition of CO to H_2

greatly retards the reaction of adsorbed formate with H_2. The reason is that CO chemisorbs strongly on the Rh site and as a results reduces the extent of dissociative adsorption of H_2.

The appearance at the beginning of the reaction of the weak band at 1770 cm^{-1}, which is very near to the C–O stretching vibration of molecularly adsorbed HCOOH, indicates that in the presence of a large excess of H_2 the reaction

$$HCOO_{(a)} + H_{(a)} = HCOOH_{(a)} \quad (1)$$

occurred, and a small amount of molecularly bonded HCOOH existed on the surface. An alternative explanation is that one of the surface species formed during the reaction is responsible for this band but we have not yet been able to confirm this possibility.

Although the primary role of the Rh is to produce active hydrogens, we can not exclude the possibility that some of the further reactions also occur with the participation of Rh, very likely at the metal/support interphase.

It should be emphasized that the results presented showed only that the formate ion located on the support can react with activated hydrogen, and that it can not be considered a completely inactive surface species. Further measurements are required to decide whether, during the catalytic hydrogenation of CO and CO_2, the contribution of this reaction is significant or negligible compared to the reactions of other surface species intermediates formed during the catalytic processes.

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