# Role of Water Vapour in the Carbon Monoxide–Water Reaction System on an Iron Catalyst

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Fourier transform i.r. techniques have been used to identify intermediates in the reaction of CO with water vapour over an iron catalyst.

In fundamental studies on the hydrogenation of CO over iron catalysts interest has centred mainly on the interaction between hydrogen and CO;[1–5] although hydrogenation of CO by water vapour is known,[6,7] few basic studies on their specific interaction have been reported.

The iron catalyst used here was prepared by precipitation with ammonium hydroxide from aqueous iron nitrate, calcined at 400 °C for 3 h and crushed into a fine powder (ca. 400 mesh). About 1 mg of the fine powder was rubbed on to a KBr disk (ca. 190 mg), which was placed in the re-action cell and evacuated for 5 h at room temperature. The catalyst on the disk was reduced for 120 h at 400 °C in a stream of pure hydrogen (25 ml/min). CO gas (12 Torr) was then introduced into the cell at 250 °C for conditioning of the catalyst overnight and the gaseous products in the cell were then analysed by g.l.c. with Porapak-T before evacuation. This conditioning operation was repeated 3 times. Subsequently water vapour (12 Torr) was introduced into the cell at room temperature and the i.r. spectra of the catalyst and the vapour phase were measured by the Fourier transform technique.

G.l.c. analysis showed the absence of $CO_2$ gas, suggesting that the catalyst is completely reduced with hydrogen, an iron carbide is not formed, and disproportionation of CO does not occur. Furthermore, no i.r. band was found in the region expected for chemisorbed CO for the catalyst conditioned with CO at 250 °C. On the basis of these results, it can be concluded that the CO molecule is dissociated into surface carbon ($C_S$) and oxygen ($O_S$).[8,9]

A characteristic of the i.r. spectrum (Figure 1) was the appearance of the band at 3240 cm$^{-1}$ which is assigned to a surface acetylenic group. In contrast, a band at 3020 cm$^{-1}$, assigned to a =CH– group, was observed in the vapour phase. These two bands disappeared progressively with time. In addition, bands at 3090, ca. 2990, 2955, and 2875 cm$^{-1}$ were found, assigned to the asymmetric and symmetric stretching vibrations of =CH$_2$ and –CH$_3$ fragments, respectively. In Figure 1, these bands are compared with the spectrum of authentic methyl vinyl ether.

Figure 2 shows the spectra resulting from the interaction between the catalyst and $D_2O$. The spectrum of the surface showed a band at 2390 cm$^{-1}$, corresponding to the =CD group. Moreover, in the range 1800—1400 cm$^{-1}$, which is the range for rotation–vibration of $H_2O$, a band was found at 1640 cm$^{-1}$, which was assigned to the –C=C– stretching vibration of the vinyl group by comparison with the spectrum of methyl vinyl ether. In the $H_2O$ system, a broad band appeared at 1250 cm$^{-1}$. All assignments are summarized in Table 1. It is concluded that the surface compound is acetylenic and the compound in the vapour phase is methyl vinyl ether.

In a dynamic L.E.E.D. study, Kesmodel et al.[10] deduced that ethylidyne was formed on a Pt surface. The present note reports the corresponding formation of a acetylenic group on an iron surface. Together with previous reports,[8,9] the present note enables us to propose a mechanism for product formation on an iron catalyst, which is summarized in equations (1)—(3).
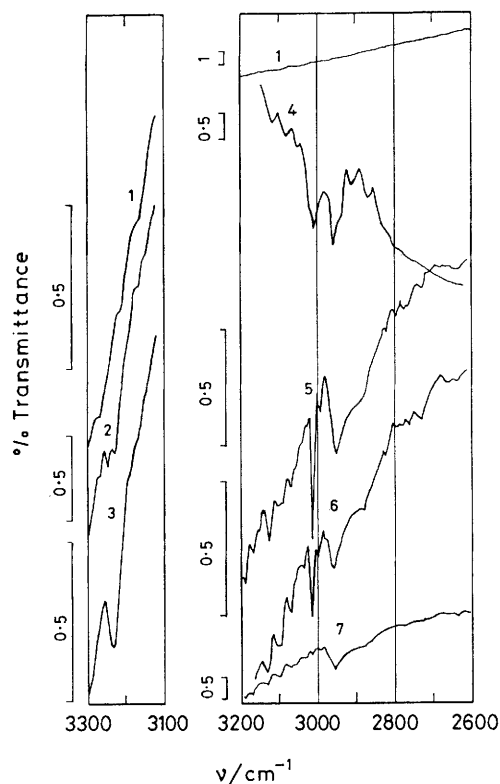


**Figure 1.** I.r. spectra of surface species on the catalyst and compound in the vapour phase (H$_2$O system): 1, background; 2, spectrum of surface after 30 min; 3, spectrum of surface after 24 h; 4, authentic methyl vinyl ether in vapour phase; 5—7, spectrum of vapour phase: 5, after 30 min; 6, after 24 h; 7, after 170 h.
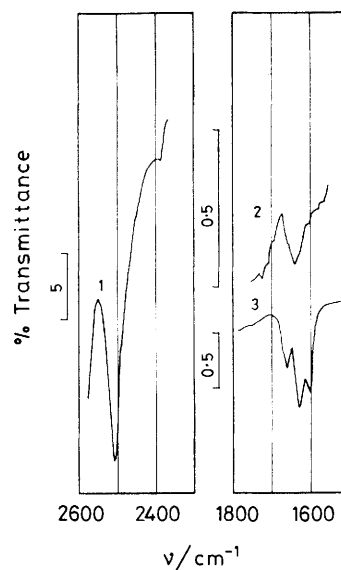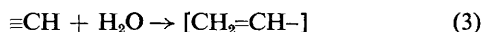


**Figure 2.** I.r. spectra of surface species and the vapour phase (D$_2$O system): 1, species on catalyst surface; 2, compound in the vapour phase; 3, authentic methyl vinyl ether.

**Table 1.** I.r. frequencies and assignments for compounds on Fe and in the vapour phase.

| Compound | $\nu$/cm$^{-1}$ | Assignment | |
|---|---|---|---|
| Surface | 3240 | $\equiv$CH | str. |
| Vapour phase | 3090 | =CH$_2$ | asym. str. |
| | 2990 | =CH$_2$ | sym. str. |
| | 3020 | =CH– | str. |
| | 2955 | –CH$_3$ | asym. str. |
| | 2875 | –CH$_3$ | sym. str. |
| | 1640 | –C=C– | str. |
| | 1250 | C–O–C | str. |

$$CO \rightarrow C_s + O_s \tag{1}$$

$$C_s + H_2O \rightarrow \; \equiv CH \tag{2}$$

$$\equiv CH + H_2O \rightarrow [CH_2{=}CH{-}] \tag{3}$$

Equation (2) shows the formation of the key acetylenic species on the surface and equation (3) shows its propagation. For methyl vinyl ether formation, methoxy-groups would be required to be formed on the surface; however, these could

not be detected. Nonethless, a potentially important role for water in its interaction with carbon monoxide on iron catalysts has been identified.

## References

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