High-pressure I.R. Spectroscopic Evidence of Acetyl and Acetate Species Directly Formed in CO–H_2 Conversion on SiO_2-Supported Rh and Rh–Mn Catalysts

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By *in situ* high-pressure i.r. spectroscopy acetyl [MeCO] as a possible intermediate for C_2-oxygenates and acetate surface species are observed over Rh/SiO_2 and Rh–Mn/SiO_2 catalysts in a CO–H_2 reaction (CO/H_2 = 0.5, 30—50 kg/cm^2, 230—270 °C).

C_2-Oxygenated compounds such as EtOH, MeCHO, and $MeCO_2H$ have been catalytically produced in a high-pressure CO–H_2 reaction over supported Rh catalysts. Addition of metal additive such as Mn and Fe to Rh/SiO_2 provided marked modifying effects on selectivity and activity for the formation[1] of C_2-oxygenates. We have also reported previously that Rh carbonyl cluster-derived catalysts prepared with some promoting metal oxides such as ZrO_2 and La_2O_3 catalysed preferentially the synthesis of ethanol.[2] To elucidate the promoting role of those metal additives and oxide-supports, we conducted high-pressure i.r. spectroscopic studies on the surface species formed in CO–H_2 conversion over several Rh supported catalysts.

In homogeneous solutions, Rh–I and Co–I carbonyl complexes catalysed homologation reactions consisting of MeOH + CO and MeOH + CO + $2H_2$ to produce $MeCO_2H$ and EtOH and MeCHO, where the acetyl [MeCO] species has been proposed as a reaction intermediate.[3]

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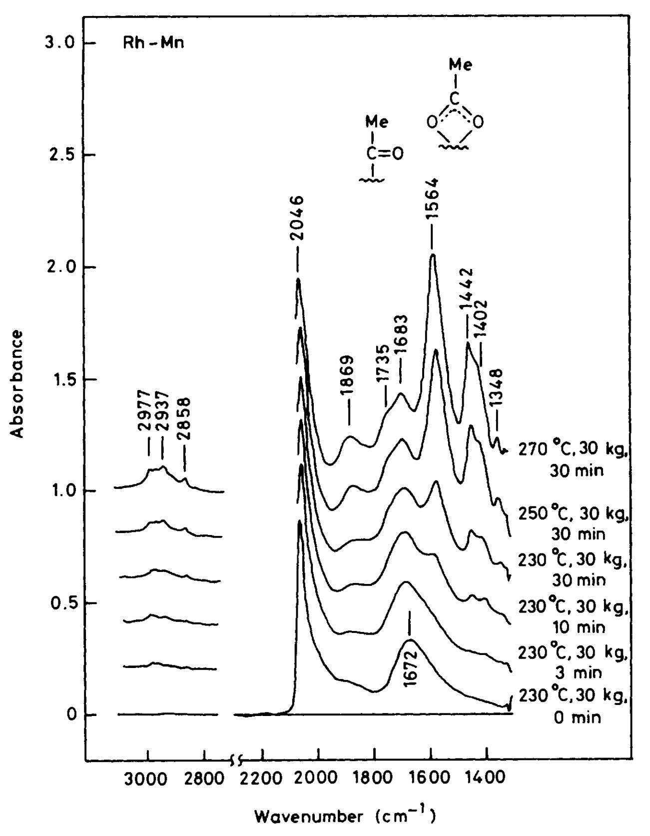


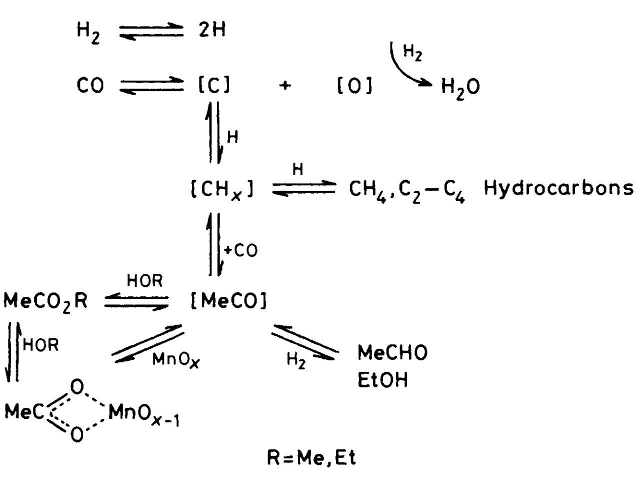
Figure 1. High-pressure i.r. spectra of adsorbed species formed in CO–H_2 conversion at 30 kg/cm^2, 230—270 °C over Rh–Mn(1 : 1)/SiO_2 catalyst. CO/H_2 = 0.5 vol. ratio.

We report here the first i.r. spectroscopic evidence of acetyl as a possible intermediate for C_2-oxygenated products and an acetate surface species, directly formed from CO and H_2 over Rh/SiO_2 and Rh–Mn/SiO_2 catalysts.

Rh/SiO_2 (4.0 wt%) and Rh–Mn (1 : 0.1—1 atomic ratio)/SiO_2 catalysts were prepared by conventional coimpregnation of $RhCl_3{\cdot}3H_2O$ and/or $MnCl_2{\cdot}4H_2O$ from ethanol solutions, depositing on SiO_2 gel (Davison #57 pellet, and Aerosil-300 powder, 280—300 m^2/g). Impregnated samples were dried and reduced in flowing H_2 by temperature-programmed heating up to 400 °C. The sizes of Rh metal in the resulting catalysts were estimated by CO-chemisorption and transmission electron microscopy, which averaged 20—40 Å for both catalysts.

Independently we found that the pelletized Rh/SiO_2 and Rh–Mn/SiO_2 catalysts produced the C_2-oxygenated compounds, mainly consisting of MeCHO and $MeCO_2H$ with 50—70% selectivity based on carbon in a 20 kg/cm^2 CO–H_2 reaction (CO–H_2 = 0.5, gas hourly space velocity 6000 h^{-1}, 250 °C) and methane as a by-product. The addition of Mn to Rh (Mn–Rh = 0.1—1 : 1) enhanced the rates of CO–H_2 conversion nearly 10 times, with similar C_2-oxygenated product selectivity, compared to the Rh/SiO_2 catalysts.

High-pressure i.r. spectra were recorded under a 0—50 kg/cm^2 CO–H_2 flow (300—500 ml/min) at 230—270 °C using a double-beam Fourier transform-i.r. spectrometer (JEOL JIR-100) with computer-processing analysis. The sample wafer (disk diameter 20 mm; 70 mg) of each catalyst was mounted in the specially designed high-pressure i.r. cell[4] with CaF_2 windows, having a minimum path length (*ca.* 1.5 mm) using packing KBr-rod spacers. Upon introducing a mixture of CO and H_2 (1 : 2 volume ratio; 30 kg/cm^2) at 230 °C onto the freshly reduced catalyst sample of Rh–Mn/SiO_2, (as shown in Figure 1), a broad but distinct band first appeared at 1672 cm^{-1}, followed by two other intense bands at 1564 and 1442 cm^{-1}, the intensities of which gradually increased until a stationary-state of the CO–H_2 reaction was reached. In the region of 3000—2800 cm^{-1} three weak bands appeared at 2977, 2937, and 2858 cm^{-1}, possibly assigned to ν(Me) and ν(CH_2) of surface hydrocarbons. On the other hand, the bands at 2046 and 1869 cm^{-1} were assigned to chemisorbed linear and bridged carbonyls, respectively. By replacing the CO–H_2 mixture with H_2 (1 atm) at 270 °C, the band at 1672—1683 cm^{-1} rapidly decreased and disappeared in 5 minutes. The latter two distinct bands, which decreased rather slowly on treatment with H_2 at 270 °C, were assigned to a bidentate acetate, possibly attached to the Mn oxide of the Rh–Mn catalyst.‡ This is reasonably confirmed by the bands of $Mn(MeCO_2)_2{\cdot}4H_2O$ in a KBr disk [ν(C=O) 1564, ν(C–O) 1434 cm^{-1}]. The band of interest at 1672 cm^{-1}, which is sensitive to hydrogen reduction, could be assigned to ν(C=O) of the acetyl species formed in CO–H_2 conversion over the Rh–Mn catalyst. This assignment is also confirmed by comparison with some related organometallic acetyl compounds such as $Rh(MeCO)Cl(I)(PBu^n{}_3)_2$, ν(C=O) 1670 cm^{-1}; $Rh(MeCO)Cl_2(CO)(PMe_2Ph)_2$, 1655 cm^{-1},[5a] $[Rh_6(CO)_{15}(RCO)][NMe_4]$ (R = Et,Pr),[5b] 1655—1670 cm^{-1}; and $Ir(MeCO)Cl_2(CO)(PEt_2Ph)_2$, 1639 cm^{-1}.[5c] The band around 1735 cm^{-1} which appeared in the CO–H_2 reaction is assigned to acetaldehyde which is physically adsorbed on the catalyst.



Scheme 1

In addition to this, we have conducted scavenging studies of the surface species by a pulse-feed of methanol onto the Rh–Mn catalyst in a steady-state CO–H_2 reaction at 230 °C; the yield of methyl acetate was abruptly enhanced, whereas those of MeCHO and EtOH remained fairly constant, implying that the acetate species might accumulate over the Rh–Mn catalyst. These results suggest that it was the acetyl species first formed directly from CO and H_2 over the Rh supported catalysts, which was converted by hydrogen into acetaldehyde and ethanol, and a part of which was also

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‡ Manganese in the Rh–Mn/SiO_2 catalyst exists in a higher valence metal oxide such as MnO, as previously observed, ref. 1b, by means of e.s.r. spectrometry.

transformed in the reaction with surface Mn-oxide into Mn-acetate.

In the case of the Rh/SiO_2 wafer sample, we have also observed a distinct band at 1650 cm^{-1} (rather weaker in comparison with those on the Rh–Mn catalyst), possibly assigned to acetyl species formed on Rh. The other three bands at 1749, 1460, and 1381 cm^{-1} were assigned to a silyl acetate [MeC(:O)–O–Si≡], possibly attached with surface silanol groups ≡Si–OH of the silica gel support under conditions of $CO/H_2 = 0.5$, 50 kg/cm^2, 270 °C.

In conclusion, as we have previously suggested[6] on consideration of the mechanism for C_2-oxygenated product formation over the $Rh_4(CO)_{12}$ derived catalysts, C_2-oxygenated compounds such as MeCHO and EtOH possibly come from an acetyl intermediate formed by CO insertion onto the surface hydrocarbons [Me] and/or [CH_2], which are derived from CO dissociation over Rh metal surface. Manganese oxide, localized in the vicinity of Rh metal, may stabilize an acetyl species formed on Rh, which is converted by hydrogen into acetaldehyde and ethanol, and spills over manganese oxide to form Mn-acetate, as shown in Scheme 1.

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References

1 (a) M. M. Bhasin, W. J. Bartley, P. C. Ellgen, and T. P. Wilson, *J. Catal.*, 1978, **54**, 120; (b) T. P. Wilson, P. H. Kasai, and P. C. Ellgen, *ibid.*, 1981, **69**, 193.

2 M. Ichikawa, *J. Chem. Soc., Chem. Commun.*, 1978, 566; *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2268, 2273.

3 G. Booth and J. Chatt, *J. Chem. Soc. A*, 1966, 634; R. W. Glyde and R. J. Mawby, *Inorg. Chem.*, (1971), **10**, 854.

4 Unpublished results.

5 (a) A. J. Deeming and B. L. Shaw, *J. Chem. Soc., A*, 1969, 597; (b) P. Chini, S. Martinengo, and G. Garlashelli, *J. Chem. Soc., Chem. Commun.*, 1972, 709; (c) G. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc., A*, 1967, 604.

6 M. Ichikawa and K. Shikakura, *Stud. Surf. Sci. Catal.*, 1981, **7**, 925; M. Ichikawa, K. Shikakura, K. Sekizawa, and M. Kawai, *J. Mol. Catal.*, 1981, **11**, 157.