Mechanism of Acetaldehyde Formation from the Carbon Monoxide–Hydrogen Reaction below Atmospheric Pressure over Supported Rh Catalysts

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The mechanism of acetaldehyde formation from the CO + H_2 reaction was examined by the isotopic tracer method using ^{13}CO and $C^{18}O$; the reaction takes place in two steps: (i) CO insertion into C_1 species which are the reaction intermediates for both hydrocarbons and acetaldehyde and (ii) subsequent formation of acetate ion in which one oxygen atom is supplied from the support, finally producing acetaldehyde.

The hydrogenation of carbon monoxide over transition-metal catalysts produces both hydrocarbons and oxygenated compounds such as alcohols and aldehydes. The mechanism of hydrocarbon formation has been investigated by many workers.[1—5] These results strongly suggest that surface carbon formed by the dissociation of CO is an intermediate for hydrocarbon formation. On the other hand, the mechanism of the formation of oxygenated compounds has not been clarified yet. Recently, Katzer *et al.*[6] and Tamaru *et al.*[7] have demonstrated that methanol is produced *via* hydrogenation of non-dissociated CO. Takeuchi and Katzer[8] have also studied the mechanism of ethanol formation by use of a 50 : 50 mixture of ^{13}CO and $C^{18}O$, and proposed a rather complicated mechanism involving CO insertion into an adsorbed carbene species followed by isotopic scrambling in the adsorbed intermediate. However, they did not distinguish between the methyl and hydroxymethylene carbon atoms.

In the present study, we have investigated the mechanism of acetaldehyde formation by the isotopic tracer method. We could distinguish between the carbon isotope distribution in the methyl group of acetaldehyde and that in the formyl group from the mass spectral fragmentation pattern; we found that acetaldehyde is produced *via* CO insertion into C_1 intermediates common to hydrocarbons and subsequent formation of acetate ion.

The catalysts were prepared by impregnating aqueous solutions of metal chlorides ($RhCl_3$, or a mixture of $RhCl_3$ and $MnCl_2$) onto SiO_2 (Aerosil). After impregnation, the catalysts (5 wt% Rh) were dried in air at 383 K for *ca.* 12 h. Then they were put in a U-shaped glass reactor, which was connected to a closed gas circulation system, and dried by air circulation at room temperature with a liquid nitrogen cold trap for *ca.* 15 h prior to reduction by hydrogen at 473—723 K for several hours. The hydrogenation of CO was carried out in the circulation system with a liquid nitrogen cold trap. The reaction products were analysed and separated into components by gas chromatography, the isotope distributions being determined by a quadrupole mass filter. In order to facilitate the mass analyses of the hydrocarbons, the separated hydrocarbons were oxidized to CO_2 over Pd black and the carbon isotope distribution in the CO_2 was measured.

Before isotopic experiments, the catalysts had been used repeatedly for the hydrogenation of CO and had shown stable activity. The selectivities for the CO + H_2 reaction at 453 K (in carbon efficiency, %) were as follows: methane, 24; $C_{>1}$ (hydrocarbons higher than methane), 63; acetaldehyde, 12; ethanol, 0.4 for Rh/SiO_2; methane, 13; $C_{>1}$ 59; acetaldehyde, 17; ethanol, 11 for $Rh–Mn/SiO_2$ (Mn/Rh = 1.5). Manganese was effective for improving the selectivity for ethanol formation.

The experimental procedure for the experiments using ^{13}CO (90% purity) was as follows: (i) the ^{13}CO + H_2 reaction was carried out at 393 K for 3.5 h over freshly reduced Rh/SiO_2; (ii) the catalyst was cooled to room temperature and sufficient ^{12}CO was introduced to replace the molecularly adsorbed ^{13}CO; (iii) the ^{12}CO + H_2 mixture was introduced, and the catalyst was rapidly heated to 393 K; (iv) the variation with time of the ^{13}C distribution in the products was analysed. As shown in Table 1, the ^{13}C distribution in the methyl group of acetaldehyde exhibited almost the same behaviour as the ^{13}C distributions in the hydrocarbons and could be extrapolated to the purity of the ^{13}CO used at the initial stage of the reaction. In contrast, the ^{13}C distribution in the formyl group of acetaldehyde was markedly different from the distributions in the hydrocarbons and decreased rapidly to the natural abundance of ^{13}C (1.1%). This indicates that during the steady-state CO + H_2 reaction, there exist common C_1 intermediates through which hydrocarbons and the methyl group of acetaldehyde are formed, and acetaldehyde is produced *via* CO insertion into these C_1 intermediates.

In order to study the nature of the active site for the formation of acetaldehyde, the reaction of $C^{18}O$ (99% purity) + H_2 was carried out at 423 K over freshly reduced Rh/SiO_2 and the ^{18}O distributions in the reactant and products were measured. The results are shown in Table 2. During the reaction the ^{18}O distribution in CO was constant at 99%, but that in acetaldehyde was nearly 50% at the initial stage of the reaction and gradually increased. These results suggest that the intermediates which form acetaldehyde *via* CO insertion

Table 1. Carbon isotope distribution in products during the ^{12}CO + H_2 reaction at 393 K over the Rh/SiO_2 catalyst after ^{13}CO + H_2 reaction at 393 K for 3.5 h.

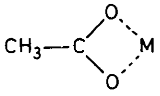
CO conversion[a] /(ml at S.T.P.)	% ^{13}C distribution in products			
			CH_3CHO	
	CH_4	$C_3' + C_3$[c]	CH_3	CHO
0.08	—[b]	—[b]	84	10
0.50	33	32	43	3
1.39	17	20	23	2
3.34	8	10	13	2

[a] P° = 240 Torr, H_2/CO = 1, 3.1 g of catalyst. [b] Not determined owing to the small amounts of products. [c] C_3' = propene and C_3 = propane.

Table 2. Oxygen isotope distribution in CO and acetaldehyde during the $C^{18}O$ + H_2 reaction at 423 K over the Rh/SiO_2 catalyst.

CO conversion[a] /(ml at S.T.P.)	Amount of CH_3CHO produced /(ml at S.T.P.)	% ^{18}O distribution	
		CO	CH_3CHO
1.02	0.02	99	48
2.24	0.08	99	46
3.90	0.18	99	52
5.41	0.28	99	56

[a] P° = 170 Torr, H_2/CO = 2, $C^{18}O$ 99% pure, 0.7 g of catalyst.



(A)

into the C_1 species have an acetate ion-like structure (A), in which one oxygen atom is supplied from CO and the other from the support, and that these intermediates are hydrogenated to acetaldehyde before further exchange reactions of oxygen with the support take place.

For the manganese-doped catalyst, the activity was one third of that for Rh/SiO_2, but the acetate ions adsorbed on the catalyst under the reaction conditions could be detected by Fourier-transform i.r. spectrometry, and the ^{18}O distribution in the acetaldehyde during the $C^{18}O + H_2$ reaction decreased to *ca.* 20% of that at the initial stage of reaction. These results suggest that manganese stabilizes the acetate intermediates just as sodium stabilizes formate ions for palladium catalysts,[9] and promotes the oxygen exchange reaction with the support. The active sites for the formation of acetaldehyde are therefore located in the vicinity of the rhodium metal and the support.

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References

1 P. R. Wentrcek, B. J. Wood, and H. Wise, *J. Catal.*, 1976, **43**, 363.
2 M. Araki and V. Ponec, *J. Catal.*, 1976, **44**, 439.
3 J. W. A. Sachtler, J. M. Kool, and V. Ponec, *J. Catal.*, 1979, **56**, 284.
4 P. Biloen, J. N. Helle, and W. M. H. Sachtler, *J. Catal.*, 1979, **58**, 95.
5 Y. Kobori, H. Yamasaki, S. Naito, T. Onishi, and K. Tamaru, *J. Chem. Soc., Faraday Trans.* 1, 1982, **78**, 1473.
6 A. Takeuchi and J. R. Katzer, *J. Phys. Chem.*, 1981, **85**, 937.
7 Y. Kobori, H. Yamasaki, S. Naito, T. Onishi, and K. Tamaru, *Chem. Lett.*, 1983, 553.
8 A. Takeuchi and J. R. Katzer, *J. Phys. Chem.*, 1982, **86**, 2438.
9 Y. Kikuzono, S. Kagami, S. Naito, T. Onishi, and K. Tamaru, *Chem. Lett.*, 1981, 1249; *Faraday Discuss. Chem. Soc.*, 1981, **72**, 135.