Mechanism of Syngas Conversion into C_2-oxygenates such as Ethanol catalysed on a SiO_2-supported Rh–Ti Catalyst

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^{13}C-Labelling studies on a Rh–Ti/SiO_2 catalyst using ^{13}CO and $^{13}CH_3OH$ revealed that in a CO–H_2 reaction C_2-oxygenates such as ethanol are formed from a common precursor *e.g.* acyl, being formed by CO insertion onto surface CH_3/CH_2 moieties derived from CO dissociation and the subsequent reaction of the carbon product with hydrogen.

In comparison with other transition metal catalysts, Rh metal catalyses conversion of syngas (CO+H_2) into C_2-oxygenates such as EtOH, MeCHO, and $MeCO_2H$.[1] We have previously reported[2] that highly dispersed Rh crystallites, which are derived from carbonyl clusters, synthesize ethanol preferentially when impregnated on ZrO_2, TiO_2, and La_2O_3, while they catalyse mainly synthesis of MeOH on ZnO and MgO and synthesis of hydrocarbons on SiO_2 and Al_2O_3 at an atmospheric pressure of CO–H_2. Moreover, the addition of Mn,[3] Zr, and Ti[4] ions to Rh/SiO_2 significantly enhanced the yields of C_2-oxygenates; addition of these transition metal ions also promotes formation of the related oxygenate species from CO and H_2 on the catalyst surface.[5] Nevertheless, it is not known whether the C_2-oxygenates are formed by a Fischer–Tropsch type chain-growth and/or an alcohol homologation process, similar to homogeneous catalysis by Co and Rh complexes,[6] which show Schulz–Flory distribution.[7] Consequently, to understand the basic mechanism of C_2-oxygenate formation in a CO–H_2 reaction catalysed by heterogeneous Rh catalysts, we have conducted ^{13}C-labelling studies employing enriched ^{13}CO and $^{13}CH_3OH$ on a Rh–Ti/SiO_2 catalyst. We report here that in all the ^{13}C-tracer experiments the results indicate selective incorporation of ^{13}C-enriched surface carbon only at the methyl carbon of C_2-oxygenates such as ethanol and essentially none at the carbonyl-derived fragment –CH_2OH and –CHO, and confirm a minor or negligible contribution of the methanol homologation process to form C_2-oxygenates, which contrasts that proposed previously by Katzer *et al.* on Rh/TiO_2 catalyst.[8]

Labelling studies using enriched ^{13}CO (99% enrichment) and $^{13}CH_3OH$ (90%), purchased from Amersham Int. Co., were performed at an atmospheric pressure of CO–H_2 on SiO_2-supported Rh–Ti catalyst. An all-glass closed circulating vessel equipped with a U-type tubing reactor was used and operated in a flow mode. Rh–Ti (1:1 atomic ratio; Rh 4.6 wt% loading on SiO_2) catalyst (2.5 g) was charged in the reactor. The catalyst was conventionally prepared by coimpregnation of $RhCl_3\cdot 3H_2O$ and $TiCl_4$ from methanol solution onto SiO_2 gel (Davison No. 57, *ca.* 20 mesh, 280 m^2/g) and was subsequently reduced in H_2-flow at 400 °C. The ^{13}C-isotopically enriched oxygenated products from the CO–H_2 reaction were collected by dissolving in cooled water (2—5 ml, 5 °C) and analysed separately by means of a g.c.-mass spectrometer (JEOL JMS-DX300) with g.c. on Chromosorb 101 (2 m, 135 °C) and 3% poly(ethylene glycol) 20 M (3 m) columns. Gas-phase analysis for CH_4, CO, and CO_2 was also performed by mass spectrometry (SHIMADZU-QP 1000) with g.c. on an active carbon 1 m column.

The ^{13}C-tracer experiments were conducted on freshly reduced Rh–Ti/SiO_2, which had been treated with ^{13}CO to

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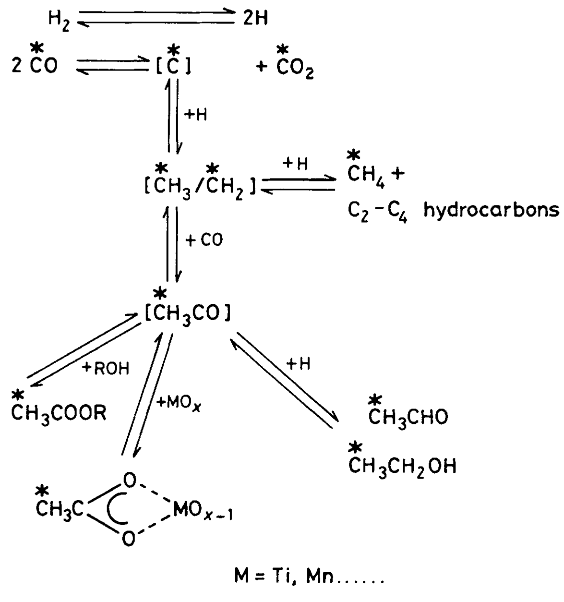
Table 1. Isotopic composition of MeOH, EtOH, and AcH in CO–H_2 reaction over the Rh–Ti/SiO_2 catalyst labelled with ^{13}C-carbon deposited by ^{13}CO dissociation. Rh: 4.6 mmol/5 g-cat.

Run	$[^{13}C]^a$ (mmol)	Reaction time^b /min	MeOH/%		EtOH/%			AcH/%	
			CH_3OH	$^{13}CH_3OH$	CH_3CH_2OH	$^{13}CH_3CH_2OH$	$^{13}CH_3{}^{13}CH_2OH$	CH_3CHO	$^{13}CH_3CHO$
1	0.9	20	100	0	65	34	1	79	21
		25	99	1	76	22	2	85	15
		38	100	0	84	16	0	90	10
2	1.2	10	100	0	38	58	4	60	39
		20	99	1	61	37	2	82	17
		36	99	1	85	14	1	91	9

[a] $[^{13}C]$ Was estimated from the $^{13}CO_2$ formed in the Boudouard reaction at 200—230 °C.
[b] Flow-mode operating reaction, 1 atm, CO/H_2 0.5, 200—210 °C, specific velocity = 400 h^{-1}.



Scheme 1

enrich the surface carbide by the Boudouard reaction at 200—220 °C [$2^{13}CO \rightleftharpoons {}^{13}C + {}^{13}CO_2$] in a closed circulating reactor. The amount of ^{13}C-carbide on the Rh–Ti catalyst (^{13}C/Rh) was estimated from the $^{13}CO_2$ formed. The catalyst was subsequently exposed to ^{12}CO (1 atm, 25 °C) to exchange associatively chemisorbed ^{13}CO before introducing a mixture of ^{12}CO and H_2 (1 atm, CO/H_2 0.5 vol%, specific velocity = 400 h^{-1}) in a flow-mode; the temperature was raised to 200 °C. The products formed were dissolved in water, and sampled at a given interval during the CO–H_2 reaction. The ^{13}C compositions of each fraction were completely analysed by g.c–mass spectrometry (m.s.), the results of which are shown in Table 1. The product selectivities of EtOH, MeCHO, MeOH, CH_4, and others were 42%, 6%, 4%, 38%, and 11% (based on carbon) respectively, observed on the Rh–Ti/SiO_2 catalyst with ^{13}C/Rh 0.4. G.c.–m.s. analysis of the ethanol and acetaldehyde fractions, as shown in Table 1, indicates a significant ^{13}C-enrichment only at the methyl carbon of ethanol and acetaldehyde and a negligible enrichment at the carbonyl-derived fragments, *e.g.* –CH_2OH and –CHO. Methane in the effluent gas was formed with parallel enrichment of ^{13}C. In contrast, a trace amount of ^{13}C-labelled product was detected in all the methanol fractions. It is interesting that the % abundance of ^{13}C-labelled fractions in the ethanol and acetaldehyde, $^{13}CH_3CH_2OH$ and $^{13}CH_3CHO$, formed, could be extrapolated to above 80% at the initial reaction of $^{12}CO+H_2$ with the ^{13}C-enriched Rh–Ti surface, as shown in Figure 1. Accordingly, these results suggest that one carbon-unit, the 'methyl' of C_2-oxygenates, should come from the surface carbon, *i.e.* the CH_3/CH_2 unit is formed by CO dissociation on the Rh metal, and a subsequent insertion reaction of CO provides a common precursor of C_2-oxygenates, possibly a CH_3CO species on the catalyst. Absence of incorporation of surface carbon into the methanol fraction indicates that methanol is formed in the hydrogenation of non-dissociated CO,[9] at different sites from the formation of C_2-oxygenates. Interestingly, we found that

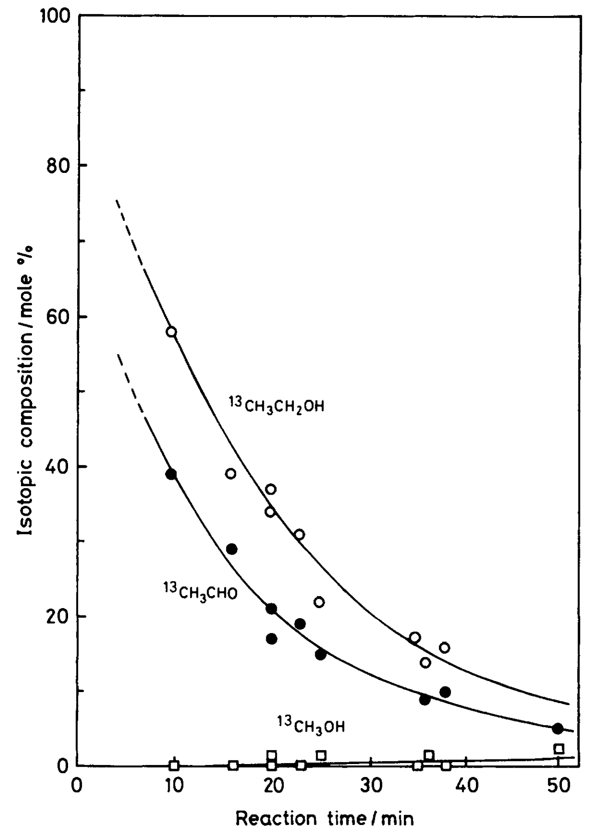


Figure 1. Isotopic composition of MeOH, EtOH, and AcH in the reaction of CO–H_2 over Rh–Ti/SiO_2 labelled with ^{13}C deposited by ^{13}CO dissociation. Rh–Ti ratio 1 : 1, ^{13}C 0.9—1.2 mmol/Rh 4.6 mmol, CO–H_2 1 : 2 vol ratio, 1 atm, 200—210 °C, specific velocity 400 h^{-1}.

Table 2. Isotopic composition of EtOH, AcH, and methyl acetate in a CO–H_2 reaction by feeding $^{13}CH_3OH$ (90%), 1.0 mmol/h, over the Rh–Ti (1 : 1)/SiO_2) catalyst. $^{13}CH_3OH$ (90%) + CO + H_2(CO/H_2 0.5) 1 atm, 205—210 °C, specific velocity = 400 h^{-1}.

	Run 1 (20 min) %	Run 2 (35 min) %	Run 3 (60 min) %
$^{13}CH_3OH$	75	70	61
CH_3OH	25	30	39
$^{13}CH_3CHO$	0	0	0
$^{13}CH_3{}^{13}CHO$	0	0	0
CH_3CHO	100	100	100
$^{13}CH_3CH_2OH$	21	27	29
$^{13}CH_3{}^{13}CH_2OH$	0	0	0
CH_3CH_2OH	79	73	71
$CH_3COO^{13}CH_3$	72	83	83
$^{13}CH_3COO^{13}CH_3$	2	1	1
$^{13}CH_3{}^{13}COO^{13}CH_3$	8	9	6

$CH_3CH_2CH_2OH$, CH_3COCH_3, $CH_3CH_2CH_2CH_2OH$, and $CH_3COOC_2H_5$ fractions were not labelled with ^{13}C during the reaction.

acetone, formed as a minor by-product in the CO–H_2 reaction, was labelled with ^{13}C as $^{13}CH_3COCH_3$ and $^{13}CH_3CO^{13}CH_3$ in almost equal mole %. This implies that the subsequent scrambling reaction proceeds between acyl and methyl species on the Rh–Ti/SiO_2 catalyst.

^{13}C-Labelled CH_3OH (90% enrichment) was introduced by controlling its feed (0.5—1 mmol/h) onto a stationary-state 1 atm CO–H_2 reaction on Rh–Ti(1 : 1)/SiO_2 catalyst. Decomposition of methanol occurred negligibly in the CO–H_2 reaction at temperatures around 220 °C. The ^{13}C compositions in each product fraction are shown in Table 2. Product ethanol was composed of labelled species *e.g.* $^{13}CH_3CH_2OH$ in *ca.* 20% incorporation of the total ethanol formed. No incorporation of ^{13}C-labelled methanol was found in any acetaldehyde, methane, or propanol fractions. Single ^{13}C-labelling in a methyl acetate fraction is from the incorporation of $^{13}CH_3OH$ in its methyl ester position. This is consistent with our previous results,[2,4,5] suggesting that acyl and acetate species are accumulated on Rh–Mn and Rh–Ti catalysts in a CO–H_2 reaction, which are transformed as methyl acetate by the transient methanol feed. Tamaru *et al.*[10] also suggested that interfacial support oxygen atoms in Rh/SiO_2 catalyst are incorporated in C_2-oxygenate formation from $C^{18}O+H_2$, indicating acetate formation, in which one oxygen atom is provided from the support. Consequently, the ^{13}C-isotopic compositions of the C_2-oxygenate fractions examined using $^{13}CH_3OH$ reveals there is a minor contribution from methanol homologation for C_2-oxygenates on the SiO_2-supported Rh–Ti catalyst, and also excludes any possibility of alcohol condensation.

In conclusion, as we have previously proposed,[2,5] based on kinetic considerations, C_2-oxygenates such as ethanol and acetaldehyde are formed *via* the essential steps in the mechanism shown in Scheme 1; dissociation of CO to carbon and oxygen, hydrogenation of surface carbon to CH_3, followed by carbonylation. This mechanism is in agreement with our observed product array in ^{13}C-labelling experiments and the existence of acyl species proposed on Rh–Mn, Rh–Ti, and Rh/SiO_2 by means of *in-situ* high pressure i.r. spectroscopic techniques.[11]

This work was supported by a National Research Development Program of the Ministry of International Trade and Industry.

Received, 16th November 1984; Com. 700

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