Cyclopropane formation during carbon monoxide hydrogenation over rhodium–ceria–silica in the presence of tetravinylsilane as probe

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The cyclic hydrocarbon, cyclopropane is obtained when carbon monoxide is hydrogenated over a silica supported rhodium catalyst, in the presence of tetravinylsilane, TVS. The cyclopropane derived from the $^{13}C_2$-labelled TVS, $Si(^{13}CH{=}^{13}CH_2)_4$, is almost entirely $^{13}C_2{}^{12}CH_6$, showing it to be formed from one vinyl of TVS and a surface C_1 species derived from CO. This finding lends support to the intermediacy of surface methylene in the Fischer–Tropsch reaction and illustrates a new synthetic potential for such reactions.

Keywords: cyclopropane; rhodium; tetravinylsilane; methylene; CO hydrogenation; isotopic labelling

1. Introduction

There has been much interest in rhodium-catalysed Fischer–Tropsch reactions since the original patents by Union Carbide workers [1] and a paper by Vannice [2] in 1975. Recent work has been summarised in papers by Yu-Hua [3], Bernal [4], and Trovarelli [5] and their coworkers, who have also built upon the observation by Ichikawa [6] and Watson and Somorjai [7], that the activity of rhodium catalysts is substantially promoted by reducible oxides, especially TiO_2, ZrO_2, and those of the lanthanides. It was also found that under some conditions the selectivity of the Fischer–Tropsch process towards oxygenates, in particular ethanol, was substantially enhanced.

As we have recently reported, addition of tetravinylsilane (TVS) or vinyl bromide to a syngas stream over a rhodium–ceria–silica catalyst (1 atm, 498 K) caused little perturbation in the distribution of the Fischer–Tropsch products [8–10]. When $Si(^{13}CH{=}^{13}CH_2)_4$ or $Br^{13}CH{=}^{13}CH_2$ was used as the probe molecule, $^{13}C_2$, but not $^{13}C_1$ or $^{13}C_3$, was incorporated into the hydrocarbons but *not*

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into the oxygenates. These data, which showed that vinyl participates in the initiation of hydrocarbon growth, and that it is not cleaved under these conditions, are consistent with our proposal that the Fischer–Tropsch polymerisation involves surface alkenyl rather than surface alkyl species [10].

We have now established that cyclopropane, a quite novel product from carbon monoxide hydrogenation, is also formed in reactions where tetravinylsilane is present.

2. Experimental

2.1. EQUIPMENT

Quantitative analysis of the reaction products was carried out by gas chromatography, using a Supelco SPB-1 (60 m × 0.53 mm × 5 μm) column. Analysis of the level of ^{13}C incorporation was by GC-MS (HP 3700-5171 A). The products were separated by a Chromosorb CPSil-5CB (50 m × 0.34 mm × 5 μm) capillary column and the fractions of the various molecular weight isomers $^{13}C_x{}^{12}C_{n-x}$ calculated by comparison with the unlabelled molecular ion envelope.

2.2. CATALYST PREPARATION

The catalyst was prepared by impregnation of the support (Davisil grade 645 silica gel) to incipient wetness in a two-stage process to give loadings of 9% CeO_2 and 4% Rh, respectively. In the first step, an aqueous solution of $Ce(NO_3)_3 \cdot 6H_2O$ (Aldrich) was added and the catalyst heated slowly to 373 K to drive off the water, this was followed by more rapid heating to 473 K. In the second impregnation step, addition of $Rh(NO_3)_3$ (Johnson Matthey, 14.07%, as a solution in 1.7 M nitric acid) was followed by slow heating to 373 K, at which temperature the catalyst was fully dried.

The catalyst (1.0 g), in a glass flow reactor (ca. 6 mm × 350 mm), was reduced under a steady stream of hydrogen (1 atm, 480 cm^3/h), by programmed heating (4 K/min) from room temperature to 673 K, it was held at 673 K (4 h) to ensure complete reduction, and was then allowed to cool in a stream of hydrogen.

2.3. SYNTHESIS OF LABELLED TETRAVINYLSILANE

Labelled TVS was prepared by a modified literature procedure [11]. Labelled vinyl Grignard was prepared by reacting vinyl bromide (99% $^{13}C_2H_3Br$, Matheson of Canada, 1.0 g) with magnesium (0.22 g) in dry tetrahydrofuran (THF) under nitrogen. The reaction was initiated with a trace of 1,2-dibromoethane. The resulting vinyl Grignard was then treated with $SiCl_4$ (0.24 g) in pentane (3.4 cm^3) and gently refluxed. Work up gave a solution of labelled TVS in THF. Pure $Si(^{13}C_2H_3)_4$ was obtained by preparative GC and analysis by GC-MS showed it to be ca. 99% $^{13}C_2$ labelled.

2.4. REACTION UNDER SYNTHESIS GAS

After reduction at 673 K, the catalyst was cooled to the reaction temperature (498 K) under hydrogen and the gas flow switched to synthesis gas (1 atm, $CO : H_2 = 1 : 2$; flow rate 480 cm^3/h). Equilibrium was reached after 1 h on stream and the products of the reaction were either sampled directly from the gas stream and analysed by gas chromatography or collected in a liquid nitrogen trap. The latter method was used to collect enough of the higher molecular weight products for detection and GC-MS analysis. The activity of the catalyst decreased with time on stream; it was regenerated periodically by heating to 673 K in a stream of hydrogen.

Two methods of addition of the labelled probe molecule (ca. 25-fold excess of CO by carbon) were used: (i) pulses of the probe were added at five minute intervals to the gas stream or, alternatively, (ii) a continuous dose of the probe was added. In each case the products were collected at low temperature (−78°C) and analysed (GC-MS). The results showed that the method of addition had very little effect on the amount of incorporation of the labelled probe, or on the overall product distribution.

3. Results and discussion

Reaction of a syngas mixture ($CO : H_2 = 1 : 2$, 500 cm^3/h) over a rhodium (4%)–ceria (9%)–silica catalyst under conditions of low conversion (3% at 1 atm and 498 K) yielded Fischer–Tropsch products up to C_{14}, with a probability of growth, α, of ca. 0.4. The majority of the hydrocarbons were linear olefins, but some linear alkanes and branched olefins, together with some oxygenates (ethanol, acetaldehyde, methanol and traces of propanol) were produced (table 1).

Tetravinylsilane was initially chosen to probe the carbon monoxide hydrogenation reaction since it was expected to perturb the system least, as silicon-containing side-products can be expected to be absorbed into the silica support material. This appeared to be the case, and the observed distribution of Fischer–Tropsch products was scarcely changed when small amounts of TVS were added to the syngas stream, indicating that TVS did not poison (or promote) the catalyst. Only two significant differences were detected. As expected, the amount of ethane, formed by direct hydrogenation/hydrogenolysis, increased sharply (table 1). Separate experiments using a sample of pure, fully labelled $Si(^{13}C_2H_3)_4$ (99% $^{13}C_2$, made from $^{13}C_2H_3Br$), showed that the ethane formed contained substantial amounts of $^{13}C_2H_6$ which must, therefore, have arisen by hydrogenation of the TVS. Indeed, significant amounts of tetraethylsilane were detected by GC-MS. There was no corresponding rise in methane formation, nor was there any significant incorporation of $^{13}C_1$ label into other products. Thus, while the TVS is hydrogenated, C–C cleavage does not occur here.

Table 1
The products of the Fischer–Tropsch reaction over a rhodium (4%)–ceria (9%)–silica catalyst, before, during and after addition of tetravinylsilane (TVS); the effect of the amount of probe added on the product distribution (%), and formation rate (in μmol of C / g-cat h; in parentheses)

Carbon fraction	Product distribution (35 μmol/h of TVS)			Product distribution (140 μmol/h of TVS)		
	before	during	after	before	during	after
C_1	52	45.5	51	50	26.5	43
	(52.2)	(41.3)	(39.2)	(62.0)	(31.7)	(34.1)
C_2	3	10	5	5	30	7
	(8.9)	(18.8)	(7.0)	(12.8)	(71.3)	(11.3)
C_3	8	8	8.5	10	9	7
	(25.5)	(22.2)	(17.2)	(36.7)	(45.1)	(17.9)
C_4	3.5	3	3	4	4	3
	(14.2)	(11.8)	(9.7)	(19.9)	(18.1)	(9.4)
C_5	2	2	2	2	6	2
	(9.4)	(10.2)	(7.1)	(13.1)	(33.1)	(7.6)
C_6	1	1	1	1	1	1
	(7.7)	(6.9)	(6.2)	(10.2)	(6.6)	(5.1)
C_7	1	1	1	1	1	1
	(7.5)	(6.9)	(5.8)	(10.3)	(6.6)	(4.8)
MeOH + MeCHO	7	6.5	7	10	14.5	28
	(14.1)	(11.8)	(11.7)	(24.2)	(34.6)	(44.0)
EtOH	21	21	21.5	17	5	8
	(42.4)	(38.8)	(33.0)	(42.7)	(12.1)	(12.1)
cyclopropane	0	0.6	0	0	4	0.3
	0	(1.7)	0	0	(14.1)	(0.6)

The second difference was completely unexpected: cyclopropane was formed as a product of the reaction. The source of this hydrocarbon, which had not been previously observed in Fischer–Tropsch reactions, was established by the fact that it only arose with TVS as probe, and was not seen when vinyl bromide was used. Further, and most persuasively, when the cyclopropane peak from experiments using $\mathrm{Si(^{13}CH = ^{13}CH_2)_4}$ and unlabelled syngas ($\mathrm{H_2{-}^{12}CO}$) was analysed, it was found to be virtually entirely (>95%) composed of $\mathrm{^{13}C_2{}^{12}C_1H_6}$; there was only a trace of $\mathrm{^{13}C_1{}^{12}C_2H_6}$. Hence, it must derive from one $\mathrm{^{13}C_2H_3}$ of a TVS and one $\mathrm{^{12}CO}$ from the syngas.

Increasing the rate of TVS addition increased the rate of cyclopropane formation, with larger quantities of TVS (CO : TVS = 6 : 1, by carbon) giving up to 4% of the total products as cyclopropane (table 1)[#1].

A number of previous studies have reported the use of probes (such as ethene,

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[#1] Large quantities of TVS also appear to suppress the formation of ethanol and promote the formation of acetaldehyde, even though no label was found in these products when $\mathrm{Si(^{13}CH{=}^{13}CH_2)_4}$ (CO : TVS = 25 : 1, by carbon) was used as probe.

benzene, cyclohexene and cyclopentene) in Fischer–Tropsch reactions and have noted the formation of the one-carbon homologation products of the probe hydrocarbons (propene, toluene, methylcyclohexene and methylcyclopentene respectively); the formation of ring expansion products, cycloheptatriene (from benzene) and cyclohexene (from cyclopentene) was also observed. It was suggested that these reactions involved the addition of a C_1 surface species, presumably surface methylene, to a double bond [12]; however, no definitive information concerning the exact source of that species could be derived from the evidence available.

The formation of $^{13}C_2{}^{12}C_1H_6$ when $Si(^{13}CH{=}^{13}CH_2)_4$ was the probe makes it clear that the surface methylene, CH_2, derives from the synthesis gas, and that it is incorporated into organic products. This process begins to resemble the cyclopropanation of olefins by sources of methylene (or *carbene*), such as diazomethane; indeed the homogeneous catalysis of the reaction of organic diazo compounds ($RCHN_2$) with olefins by rhodium salts is well-known [13]. Such reactions occur with particular facility for vinylsilanes to give the appropriate cyclopropylsilane [14], however, the use of H_2–CO as a source of CH_2 in this sense is unprecedented.

A route for cyclopropane formation that is consistent with our data involves the cyclopropanation of vinylsilane by a surface (i.e. rhodium-bound) methylene, followed by cleavage of the C–Si bond by a surface hydride to release the cyclopropane. This path is an alternative to the reaction of surface methylene with surface (i.e. rhodium-bonded) vinyl, which we have shown leads to linear homologation to give higher alkenes [8]. Were this to be the route to cyclopropanes (for example, if the cyclopropanes were intermediate in the homologation) then vinyl bromide should be equally effective in cyclopropanation. In fact in contrast to TVS, vinyl bromide is much more effective in linear homologation and quite inactive for cyclopropanation. Therefore, it is also consistent with our data that the transfer of vinyl to rhodium from TVS occurs with greater difficulty than from vinyl bromide.

4. Conclusion

Addition of small amounts of tetravinylsilane (as a source of vinyl) to a stream of syngas over rhodium–ceria–silica has no marked effect on the course of the Fischer–Tropsch reaction. However, in addition to the normal Fischer–Tropsch hydrocarbon products, some cyclopropane is now formed. When $Si(^{13}CH{=}^{13}CH_2)_4$ is used as probe, the cyclopropane formed is almost entirely $^{13}C_2{}^{12}CH_6$. It arises from the $^{13}C_2$ of one vinyl and the carbon of one ^{12}CO, and reveals more detail about the intimate mechanism of syngas hydrogenation. Such reactions indicate a potential for new types of organic syntheses.

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