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Mechanistic Studies of Methylene Chain Propagation in the Fischer–Tropsch Synthesis

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Probe molecules designed to generate methylene (CH_2) were added to rhodium-, ruthenium-, and cobalt-catalysed Fischer–Tropsch reactions to investigate the mechanism of hydrocarbon chain growth during CO hydrogenation. Statistical incorporation of $^{13}CH_2$ derived from $^{13}CH_3NO_2$ or $^{13}CH_2N_2$ occurred during the hydrogenation of ^{12}CO over Co/SiO_2 catalysts (1 atm, 523 K) to give the isotopically mixed alkenes, $^{13}C_x\,^{12}C_{n-x}H_{2n}$ and the alkanes derived from them. These results show that there is complete scrambling of ^{12}C and ^{13}C labels over cobalt; the levels of $^{13}CH_2$ incorporation from the probe are consistent with a process which involves the participation of methylene groups in the chain propagation step. The data are also consistent with the alkenyl cycle proposed earlier for the Fischer–Tropsch reaction. By contrast, the same probe experiments over Rh/SiO_2 or $Rh/Ce/SiO_2$ catalysts gave the isotopically distinct $^{12}C_nH_{2n}$ (from ^{12}CO hydrogenation) and $^{13}C_nH_{2n}$ (from oligomerisation of the $^{13}CH_2$ from the $^{13}CH_3NO_2$ or $^{13}CH_2N_2$ probes), and there was very little of the isotopically mixed alkenes, $^{13}C_x\,^{12}C_{n-x}H_{2n}$ and the alkanes derived from them. Similar reactions over Ru/SiO_2 exhibited behaviour intermediate between cobalt and rhodium. Significant amounts of substituted amines and nitrile compounds are additionally formed when nitromethane is used as a probe; ^{13}C incorporation into the nitrogenous products was observed when $^{13}CH_3NO_2$ was used as probe. The relative ability of nitromethane to produce N-containing compounds decreases in the order rhodium > ruthenium > cobalt. There was little ^{13}C incorporation into the oxygenates (methanol, ethanol, and acetaldehyde) when $^{13}CH_2N_2$ or $^{13}CH_3NO_2$ was used as a probe.

INTRODUCTION

An industrially useful technology is the catalytic conversion of syn gas (CO/H_2), which can be derived from coal, natural gas, or naphtha, into synthetic liquid fuels (Fischer–Tropsch reactions) (1). There has recently been considerable interest in understanding the hydrogenation of CO in order to achieve higher selectivity to useful compounds.

Fischer–Tropsch reactions are typically carried out by passing syn gas over a supported metal catalyst at temperatures ≥473 K, at atmospheric pressure or above. The products consist principally of alkenes and alkanes, together with some alcohols, aldehydes, and ketones. The product distribution is influenced by the catalyst composition and the conditions of the catalysis. The primary hydrocarbon products are 1-alkenes which may then undergo isomerisation and/or hydrogenation to produce internal alkenes and alkanes.

Analysis of the molecular weight distribution of the Fischer–Tropsch hydrocarbons shows that Anderson–Schulz–Flory (2) polymerisation kinetics are followed, consistent with a process involving the oligomerisation of C_1 intermediates. Fischer and Tropsch originally suggested that the hydrocarbons were produced via the surface polymerisation of methylene groups, formed by sequential hydrogenation of surface carbide, generated from the decomposition of CO on the metal surface with concomitant water loss. Since then many proposals have been made for the mechanism of C–C bond formation. For example, Anderson and co-workers (3) suggested a scheme based on a self-condensation of surface hydroxycarbene intermediates, generating oxy-species, which acted as precursors for *both* hydrocarbon and oxygenate formation. An alternative mechanism by Pichler and Schulz (4) proposed that C–C bond formation in the propagation proceeds via insertion of CO into a metal–alkyl bond, a reaction well known in molecular homogeneous systems. The classic experiments by Brady and Pettit (5) confirmed that methylene was a key intermediate in hydrocarbon chain growth. They, and Biloen and Sachtler (6), proposed that the polymerisation of surface methylene was initiated by surface alkyl (or hydride) groups. Thus surface alkyls were the chain carriers and the polymerisation chain was terminated by a β-elimination which released 1-alkenes, the primary products.

Our early work on the mechanism of CH_2 oligomerisation during CO hydrogenation stemmed from studies of complexes of the type $[(\eta^5\text{-}C_5Me_5)_2Rh_2(CH_2)_2(Me)(MeCN)]^+$ which readily decompose to give propene (7). These complexes can be viewed as models of portions of the surface of a Fischer–Tropsch catalyst during a

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polymerisation reaction. Decomposition studies of various isotopomers of the rhodium complex suggested that formation of the propene involved σ-vinyl, (σ-CH=CH$_2$), rather than σ-alkyl intermediates. In fact, quite a number of authors had previously noted that C_2 species appeared to be implicated in CO hydrogenation but without formulating any more precise mechanistic suggestions (8).

We have rationalised the special role of vinyl (and alkenyl) species in the model systems. We also have shown that for CO hydrogenation reactions over *heterogeneous* rhodium, ruthenium, cobalt and iron catalysts, initiated by vinyl-$^{13}C_2$ probe molecules, the levels of $^{13}C_n$ incorporation found in the hydrocarbon products are consistent with a process in which the propagating surface methylene reacts with surface *alkenyl* rather than *alkyl* groups (9–12). In this new alkenyl mechanism, we have suggested that chain growth is initiated by the coupling of surface vinyl with surface methylene groups.

The importance of surface methylene in CO hydrogenation will be clear from the foregoing discussion. Various techniques have been used to demonstrate the intermediacy of surface methylene, including surface spectroscopy, probe molecule studies, and chemical trapping experiments. The decomposition reactions of various suitable precursors, such as diazomethane, diazirine, ketene, and dihalomethane, over metal surfaces also appear to give methylene (13). Various chemical trapping agents (such as unsaturated hydrocarbons) have also been used to scavenge methylene from surfaces during CO hydrogenation (14), and detailed surface studies have identified methylene as the key intermediate in the Fischer–Tropsch synthesis (15).

Brady and Pettit (5) investigated the addition of small amounts of (labelled) ^{13}CO to a polymerisation of (unlabelled, ^{12}C) diazomethane over a cobalt catalyst. They showed that the distribution of ^{13}C atoms in propene formed in the reaction agreed with a mechanism involving an oligomerisation of methylene (derived from diazomethane) as propagating species, as originally proposed by Fischer and Tropsch, but was inconsistent with mechanisms such as those proposed by Pichler, Schulz, and Anderson, described above. Blackmond and co-workers (16) later reported the use of nitromethane as an alternative source of methylene during CO hydrogenation.

We recently obtained unexpected results from some diazomethane probe experiments on CO hydrogenation over rhodium catalysts, which had been designed to build on the Brady–Pettit data over cobalt (5). To clear up the anomalies we extended our investigations to reactions over ruthenium and cobalt catalysts, as well as rhodium. In order not to perturb the normal CO hydrogenation reactions too greatly, we used small amounts of ^{13}C-labelled diazomethane and of ^{13}C-labelled nitromethane as methylene precursor probes in a large excess of unlabelled CO. The use of labelled probes also allows the direct detection of probe incorporation into the hydrocarbon products by mass spectral analysis at high levels of sensitivity. We here report details of our investigations; a preliminary communication on part of this work has appeared (17).

EXPERIMENTAL

Equipment

Quantitative analysis of the reaction products was carried out by gas chromatography on a Supelco SPB-1 (60 m × 0.53 mm × 5 μm) capillary column. This GC column was effective in resolving individual products up to C_7 but we experienced some difficulty in resolving propene and propane; hence only partial data are available for the C_3 hydrocarbons. The level of ^{13}C incorporation was analysed by GC–MS (HP 5890–5171 A); the products were separated on a Chrompak CPSil-5 CB (50 m × 0.32 mm × 5 μm) or a Poraplot alumina column, and the fractions of the isomers $^{13}C_x$ $^{12}C_{n-x}$ of various molecular weight calculated by comparison with the unlabelled molecular weight envelope (9). The GC–MS columns allowed clean resolution of propene and propane but had difficulty with some of the higher molecular weight hydrocarbons such as 3-hexene and hexane.

Preparation of the Rh/Ce/SiO$_2$ Catalyst

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 99.999%) was added to silica gel 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 $Rh(NO_3)_3$ (assay 10.03% in nitric acid, PGP Industries, Ireland) was followed by slow heating to 373 K, at which temperature the catalyst was fully dried.

Preparation of the Rh/SiO$_2$, Ru/SiO$_2$, and Co/SiO$_2$ Catalysts

The catalyst was prepared by impregnation of the support (Davisil grade 645 silica gel) to incipient wetness to give a loading of 4% Rh, 4% Ru, or 4% Co. Aqueous solutions of $Rh(NO_3)_3$ (assay 10.03% in nitric acid, PGP Industries, Ireland), of $Co(NO_3)_2 \cdot 6H_2O$ (Fisons, AR reagent), or of $RuCl_3 \cdot xH_2O$ (assay 41.83%, PGP Industries, Ireland) in methanol, were added to the support and were slowly heated, with frequent stirring (to 373 K for Rh, Co; 353 K for Ru) at which temperature the catalyst was fully dried.

Reaction Conditions and Catalyst Activation

The catalyst (1 g in a fixed-bed microreactor, dimensions 6 × 350 mm) was reduced under a steady stream of hydrogen (1 atm, 700 cm^3 h^{-1}), with programmed heating

(4 K min^{-1}) from room temperature to 673 K, and held at 673 K (4 h) to ensure complete reduction. The catalyst was then cooled to the reaction temperature (523 K) under hydrogen and the gas flow switched to CO–H_2 (1 : 2; 1 atm; 500 cm^3 h^{-1}). Good reproducibility, with optimum activity and selectivity, was achieved after two activation cycles of the catalyst, each involving 6 h on stream followed by reduction under hydrogen. The full activation of the catalyst was performed prior to each experiment to remove the buildup of surface carbon since the activity of the catalysts decreased with time on stream. When nitromethane was used as a probe, a further deactivation of the catalyst occurred.

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 and analysed by GC–MS. The latter method was used to collect enough of the higher molecular weight products for detection and GC–MS analysis. Quantification was achieved by calibration of the GC FID detector with standards of known molarity. For the runs with probes, the products were analysed by GC and GC–MS before, during, and after probe addition. A background GC was initially obtained to show the distribution of the products and activity. After a period of 1.5 h, the probe molecule was added to the syn gas feed stream; nitromethane was directly injected into the gas mixture through a septum and diazomethane gas was introduced by diverting the syn gas flow through the vessel which contained the diazomethane gas, prepared *in situ*. A GC analysis was performed after the probe had been added. After a further 1.5-h period, a final GC was carried out to determine the activity of the catalyst after addition of probe. In each case a 250-μl sample was collected for analysis in a gas syringe over 5 s at a predetermined time after the final pulse of the probe. Products were identified by comparison of their mass spectra with Wiley library spectra, stored in the HP ChemStation software. For a few compounds (such as hexane and 3-hexene), it was not possible to obtain good baseline separation of the peaks.

Probe Molecule Addition

Nitromethane ($^{13}CH_3NO_2$, 99% ^{13}C Aldrich) was pulsed into the syn gas stream at a rate of 1 μl every 4 min (seven pulses in total). Diazomethane ($^{13}CH_2N_2$, 99% ^{13}C) was prepared by the dropwise addition of a solution of N-methyl-^{13}C-*N*-nitroso-*p*-toluenesulphonamide (100 mg) in 2-ethoxyethanol to a stirred solution of KOH (30 mg) in 2-ethoxyethanol under an atmosphere of syn gas flowing at rate of ca. 500 cm^3 h^{-1}; this reaction formed ca. 0.3 mmol diazomethane. The generated diazomethane was cooled to 253 K using a cold finger to encourage further mixing and dilution with syn gas. The mixture of gases was swept over the catalyst for a period of 30 min at the reaction temperature. The effective ratios of probe to converted CO approximate to 1 : 10 (Rh), 1 : 15 (Ru), 1 : 9 (Co). ^{13}C incorporation into each product was then found by comparison of mass spectra taken before and during addition of probe for each product. Similar experimental procedures were employed using unlabelled ($^{12}CH_2N_2$ and $^{12}CH_3NO_2$) probe molecules.

RESULTS

CO Hydrogenation

Carbon monoxide was hydrogenated to a mixture of hydrocarbons together with some oxygenates over Rh/Ce/SiO_2, Rh/SiO_2, Ru/SiO_2, and Co/SiO_2 catalysts using a stoicheiometric mixture of syn gas. The total product activity (μmol(carbon)/gcat/h) was ca. 2200 (Rh/Ce/SiO_2), 124 (Rh/SiO_2), 4600 (Ru/SiO_2), and 2700 (Co/SiO_2). Table 1 and Fig. 1 give the formation rates of the most important products over the catalysts.

1-Alkenes and alkanes were the major hydrocarbon products over all the catalysts studied. Significant amounts of oxygenates were additionally produced over rhodium, and to a lesser extent over ruthenium and cobalt.

A plot of log(W/n) against n (W, weight fraction; n, number of carbon atoms in that fraction) gave a distribution

TABLE 1A

Product Formation Rates of Rh/Ce/SiO_2, Ru/SiO_2, and Co/SiO_2 Catalysts before Addition of $^{13}CH_2N_2$ Probe under Fischer–Tropsch Reaction Conditions at 523 K

	Product formation rate (μmol(carbon) g^{-1} h^{-1})		
Product	Rh	Ru	Co
Methane	756	1794	793
Ethene	6	42	41
Ethane	104	407	164
Propene	410	699	443
Propane	[a]	[a]	[a]
But-1-ene	48	259	258
Butane	68	196	102
trans-But-2-ene	89	138	35
cis-But-2-ene	56	137	42
Pent-1-ene	21	94	135
Pentane	40	121	105
trans-Pent-2-ene	57	83	38
cis-Pent-2-ene	25	62	31
Hex-1-ene	6	31	61
Hexane	36	74	92
trans-Hex-2-ene	33	56	37
cis-Hex-2-ene	14	35	25
Hept-1-ene	3	4	2
Hept-3-ene	9	16	28
Heptane	24	63	81
trans-Hept-2-ene	17	34	26
cis-Hept-2-ene	7	19	18
Methanol	74	3	3
Ethanol	229	2	10
Propanol	18	[b]	[b]

[a] Poorly resolved from propene.
[b] Not detected.

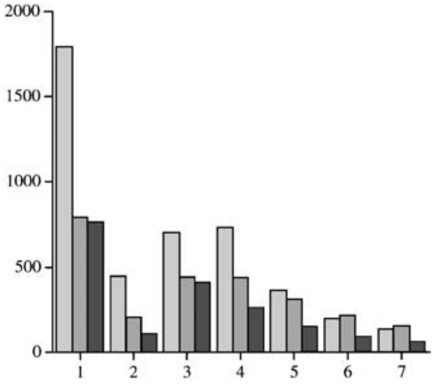

FIG. 1. Plot of product formation rate (y axis, μmol(carbon)/gcat/h against carbon number (x axis) for Ru/SiO_2 (□), Co/SiO_2 (▨), and Rh/Ce/SiO_2 (■) catalysts (oxygenated products not included).

consistent with modified Anderson–Schulz–Flory (ASF) kinetics showing enhanced C_1 and reduced C_2 products, followed by a linear decrease from C_3 to higher products indicative of a step growth oligomerisation process (Fig. 2). For the CO hydrogenation, the measured chain growth probabilities, α (C_3 to C_7 fractions), were typically 0.48 (Rh/Ce/SiO_2), 0.36 (Rh/SiO_2), 0.66 (Ru/SiO_2), and 0.61 (Co/SiO_2).

Effect of Probe Molecule Addition

Addition of small amounts of diazomethane or nitromethane probe to the CO hydrogenation led to significant changes in the product distribution. Figure 3 illustrates the distributions in the presence and absence of each of the methylene probe molecules over the various catalysts. For each of the products, three data sets are shown. The first corresponds to the product distribution under steady-state conditions, the second shows changes in the product distribution during methylene probe addition, and the third shows the return of the system to equilibrium after the probe has passed through the catalyst. The changes to the product distributions during probe addition may be summarised:

(i) addition of diazomethane or nitromethane probe caused increases in the formation rates of $C_{\geq 3}$ hydrocarbons;

(ii) addition of diazomethane enhanced C_2 product formation over all three catalysts and suppressed C_1 formation rates over ruthenium and cobalt;

TABLE 1B

Product Formation Rates of Rh/Ce/SiO_2, Ru/SiO_2, and Co/SiO_2 Catalysts before Addition of $^{13}CH_3NO_2$ Probe under Fischer–Tropsch Reaction Conditions at 523 K

	Product formation rate (μmol(carbon) g^{-1} h^{-1})		
Product	Rh	Ru	Co
Methane	861	2036	627
Ethene	3	35	31
Ethane	128	456	130
Propene	276	887	373
Propane	142	[a]	[a]
But-1-ene	34	200	204
Butane	100	191	91
trans-But-2-ene	89	153	30
cis-But-2-ene	52	142	38
Pent-1-ene	46	74	94
Pentane	59	116	85
trans-Pent-2-ene	3	90	31
cis-Pent-2-ene	24	61	49
Hex-1-ene	4	25	70
Hexane	53	68	70
trans-Hex-2-ene	32	55	30
cis-Hex-2-ene	13	32	19
Hept-1-ene	2	4	2
Hept-3-ene	10	12	22
Heptane	13	52	69
trans-Hept-2-ene	17	30	23
cis-Hept-2-ene	9	16	15
Methanol	64	8	4
Ethanol	259	5	9
Propanol	25	[b]	[b]

[a] Poorly resolved from propene.

[b] Not detected.

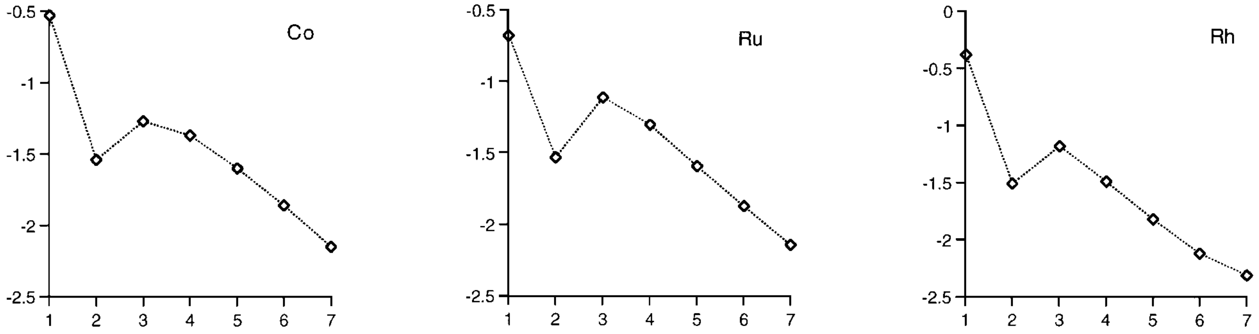

FIG. 2. Anderson–Shulz–Flory plots showing the formation of hydrocarbon products from CO hydrogenation after 1.5 h on stream; log(W/n) (y axis) against n (x axis), where W is the weight fraction having carbon number n (oxygenated products not included).

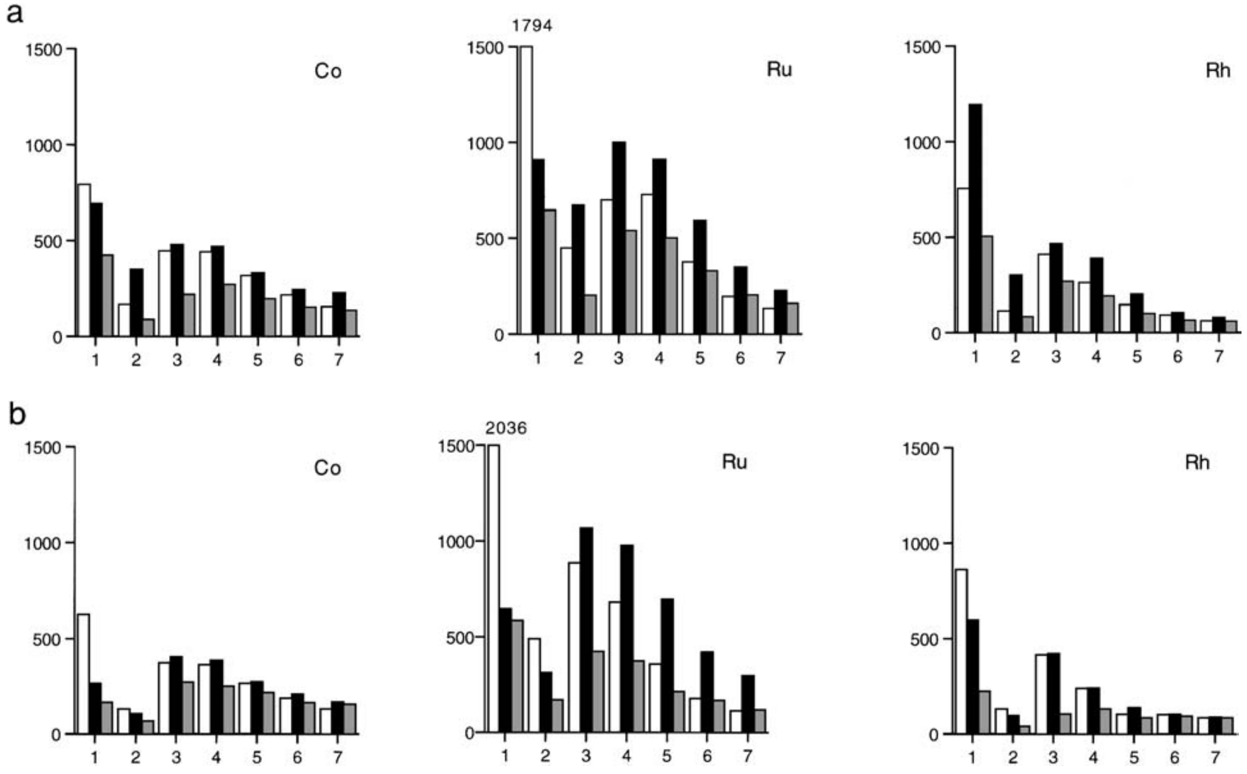

FIG. 3. Plot of product formation rate (*y* axis, μmol(carbon)/gcat/h) against carbon number (*x* axis) (□) before, (■) during, and (▨) after addition of (a) CH_2N_2 and (b) CH_3NO_2 to syn gas over Co/SiO_2, Ru/SiO_2, and $Rh/Ce/SiO_2$ catalysts at 523 K.

(iii) addition of nitromethane decreased the formation rates of C_1 and C_2 hydrocarbons and gave significant quantities of substituted amines and nitriles over rhodium and ruthenium;

(iv) the product formation rates after nitromethane addition decreased much more sharply than after diazomethane addition. The effect of probe addition can be further seen from the calculated chain growth probabilities (Table 2).

The C_n hydrocarbons formed during addition of $^{13}CH_2N_2$ and $^{13}CH_3NO_2$ to the CO hydrogenation were analysed for incorporation of $^{13}C_x$ units ($x = 0, 1, 2, \ldots, n$). The results are given as absolute percentages of $^{13}C_x$ detected (Table 3), and it is clear that the patterns of $^{13}C_x$ incorporation are similar irrespective of whether the $^{13}C_1$ units are derived from $^{13}CH_2N_2$ or $^{13}CH_3NO_2$ probes.

TABLE 2

Effect of Methylene Probe Addition on Probability of Chain Growth α

	α (before)	α (CH_2N_2)	α (CH_3NO_2)	α (after)
Co/SiO_2	0.61	0.63	0.65	0.68
Ru/SiO_2	0.66	0.68	0.69	0.69
Rh/SiO_2	0.36	0.42	0.43	0.43
$Rh/Ce/SiO_2$	0.48	0.51	0.53	0.54

DISCUSSION

CO Hydrogenation

The hydrogenation of carbon monoxide over $Rh/Ce/SiO_2$ (9, 10), Rh/SiO_2 (9, 10), Ru/SiO_2 (11), or Co/SiO_2 (12) catalysts gave hydrocarbon distributions typical for Fischer–Tropsch reactions and consistent with Anderson–Schulz–Flory polymerisation kinetics (2). The Ru catalyst exhibited the highest activity and the highest chain growth probability (α); we found that the addition of ceria to rhodium greatly increased the activity of the catalyst, but that the product distribution was largely unchanged (9). The relative reactivities of the four catalysts were ca. 37 (Ru/SiO_2) : 22 (Co/SiO_2) : 18 ($Rh/Ce/SiO_2$) : 1 (Rh/SiO_2) under similar conditions at 523 K. The major products were methane (especially over Ru), alkanes, linear 1-alkenes, and internal alkenes; some oxygenates were also produced. As had previously been reported (18), the rhodium catalyst gave larger quantities of oxygenates.

Effect of Unlabelled Probe Molecule Addition

The addition of CH_2N_2 or CH_3NO_2 probe molecules during CO hydrogenation caused increases in the quantities of $C_{\geq 3}$ hydrocarbons produced; this increase was larger when CH_2N_2 was added than when an equivalent amount of CH_3NO_2 was used. The increase in hydrocarbon formation

TABLE 3A

Percentage Incorporation of $^{13}C_n$ into Hydrocarbons and Oxygenates Formed by Addition of $^{13}CH_2N_2$ to Syn Gas over Rh/Ce/SiO$_2$, Ru/SiO$_2$, and Co/SiO$_2$ Catalysts at 523 K

Catalyst	Hydrocarbon product	Percentage incorporation							
		$^{13}C_0$	$^{13}C_1$	$^{13}C_2$	$^{13}C_3$	$^{13}C_4$	$^{13}C_5$	$^{13}C_6$	$^{13}C_7$
	Methane								
Rh		54	46						
Ru		53	47						
Co		87	13						
	Ethene								
Rh		98	2	0					
Ru		88	8	4					
Co		64	5	31					
	Ethane								
Rh		0	0	100					
Ru		0	7	93					
Co		0	15	85					
	Propene								
Rh		39	0	29	32				
Ru		71	8	12	10				
Co		19	27	37	18				
	Propane								
Rh		65	0	4	30				
Ru		56	10	9	24				
Co		61	12	14	14				
	1-Butene								
Rh		69	3	0	1	27			
Ru		71	13	5	3	8			
Co		66	18	10	2	4			
	Butane								
Rh		63	3	1	2	31			
Ru		58	13	6	5	18			
Co		70	13	9	4	4			
	trans-2-Butene								
Rh		59	2	1	0	38			
Ru		57	14	7	5	18			
Co		65	13	10	5	6			
	cis-2-Butene								
Rh		63	3	0	2	31			
Ru		57	14	7	5	18			
Co		65	13	10	5	6			
	1-Pentene								
Rh		73	4	1	0	1	21		
Ru		77	11	2	2	1	8		
Co		75	15	7	2	1	0		
	Pentane								
Rh		63	3	2	0	2	30		
Ru		80	10	2	0	1	7		
Co		66	16	12	5	1	1		
	trans-2-Pentene								
Rh		63	3	1	0	2	31		
Ru		78	11	2	1	0	8		
Co		65	16	11	4	2	1		
	cis-2-Pentene								
Rh		64	3	1	0	2	30		
Ru		79	9	1	0	0	10		
Co		65	16	11	4	2	1		
	1-Hexene								
Rh		72	3	0	0	0	2	22	
Ru		77	12	2	1	1	1	6	
Co		76	18	4	1	0	0	0	
	Hexane								
Rh		66	4	2	0	3	1	24	
Ru		76	10	1	1	2	1	9	
Co		72	15	8	3	1	0	0	
	trans-2-Hexene								
Rh		68	4	0	0	0	2	25	
Ru		78	9	2	2	2	0	7	
Co		70	16	9	3	1	0	0	
	cis-2-Hexane								
Rh		70	4	0	0	0	2	24	
Ru		78	8	2	1	2	1	8	
Co		70	16	8	3	0	0	2	
	3-Heptene								
Rh		65	5	1	0	0	0	4	25
Ru		76	10	1	2	1	1	1	8
Co		86	11	2	1	0	0	0	1
	Heptane								
Rh		69	4	0	0	0	3	2	21
Ru		78	9	1	2	1	1	1	7
Co		81	12	4	1	1	0	0	0
	trans-2-Heptene								
Rh		76	5	0	0	0	0	0	16
Ru		73	11	2	1	1	1	2	8
Co		85	8	4	2	1	0	0	0
	cis-2-Heptene								
Rh		77	5	0	0	0	1	2	15
Ru		74	10	3	1	1	1	2	8
Co		83	11	4	1	0	0	0	0
	Methanol								
Rh		91	9						
Ru		95	5						
Co		80	20						
	Acetaldehyde								
Rh		97	2	1					
Ru		94	4	1					
Co		85	10	5					
	Ethanol								
Rh		97	3	0					
Ru		98	1	1					
Co		87	5	8					

observed during probe addition suggests that both CH_2N_2 and CH_3NO_2 decompose under the experimental conditions to generate C_1 intermediates which are then involved in the hydrocarbon chain growth. It also suggests that diazomethane is better at generating the C_1 intermediate than is nitromethane. The incorporation of the probe-derived units can also be seen from the calculated α values for the product distributions (Table 2). For all the catalysts studied, addition of either CH_2N_2 or CH_3NO_2 raised the value of α, consistent with an enhancement of the propagation rate. These observations are also in agreement with earlier

TABLE 3B

Percentage Incorporation of $^{13}C_n$ into Hydrocarbons and Oxygenates Formed by Addition of $^{13}CH_3NO_2$ to Syn Gas over Rh/Ce/SiO$_2$, Ru/SiO$_2$, and Co/SiO$_2$ Catalysts at 523 K

Catalyst	Hydrocarbon product	Percentage incorporation							
		$^{13}C_0$	$^{13}C_1$	$^{13}C_2$	$^{13}C_3$	$^{13}C_4$	$^{13}C_5$	$^{13}C_6$	$^{13}C_7$
	Methane								
Rh		78	22						
Ru		84	16						
Co		88	12						
	Ethene								
Rh		87	10	3					
Ru		81	16	3					
Co		83	10	7					
	Ethane								
Rh		80	4	16					
Ru		80	13	7					
Co		85	6	9					
	Propene								
Rh		45	0	22	32				
Ru		54	19	15	12				
Co		65	14	12	8				
	Propane								
Rh		65	4	4	27				
Ru		71	17	5	8				
Co		78	9	6	7				
	1-Butene								
Rh		68	10	2	2	19			
Ru		77	11	2	2	7			
Co		70	17	6	3	5			
	Butane								
Rh		66	7	1	2	23			
Ru		77	10	2	2	9			
Co		70	17	6	3	5			
	trans-2-Butene								
Rh		61	7	2	1	30			
Ru		75	10	2	3	10			
Co		76	13	4	3	5			
	cis-2-Butene								
Rh		62	8	1	2	27			
Ru		75	10	2	3	10			
Co		75	14	4	3	5			
	1-Pentene								
Rh		71	9	3	1	2	13		
Ru		76	11	2	1	2	6		
Co		69	16	6	3	2	4		
	Pentane								
Rh		62	10	4	2	3	20		
Ru		77	12	2	1	2	6		
Co		80	10	4	2	2	3		
	trans-2-Pentene								
Rh		61	10	2	1	3	22		
Ru		74	10	2	1	2	9		
Co		86	7	2	1	1	2		
	cis-2-Pentene								
Rh		60	10	2	1	3	23		
Ru		74	11	2	1	2	10		
Co		85	8	2	2	1	3		
	1-Hexene								
Rh		67	9	2	0	1	3	17	
Ru		78	12	2	1	1	2	6	
Co		62	18	8	4	2	2	3	
	Hexane								
Rh		63	9	2	1	1	3	20	
Ru		74	11	2	1	1	2	8	
Co		80	11	4	2	1	1	2	
	trans-2-Hexene								
Rh		65	10	2	1	1	3	19	
Ru		74	11	2	1	1	2	9	
Co		85	8	2	2	1	1	1	
	cis-2-Hexene								
Rh		66	10	2	1	1	3	18	
Ru		73	11	2	1	1	2	9	
Co		82	9	3	2	1	1	2	
	3-Heptene								
Rh		60	8	2	2	2	2	3	21
Ru		75	10	2	3	1	1	1	7
Co		64	18	7	4	2	1	1	2
	Heptane								
Rh		69	8	2	1	1	3	2	13
Ru		76	11	2	1	1	1	1	7
Co		81	10	3	2	1	1	1	1
	trans-2-Heptene								
Rh		68	8	2	1	1	1	2	16
Ru		74	11	2	1	1	1	2	8
Co		84	9	2	1	1	1	1	1
	cis-2-Heptene								
Rh		67	9	2	1	1	1	3	16
Ru		75	11	2	1	1	1	2	7
Co		83	10	2	1	1	1	1	1
	Methanol								
Rh		80	20						
Ru		96	4						
Co		78	22						
	Acetaldehyde								
Rh		93	5	2					
Ru		88	4	8					
Co		89	7	4					
	Ethanol								
Rh		94	6	0					
Ru		97	2	0					
Co		90	4	6					

results reported by Pettit and by Blackmond and their collaborators (5, 16), and consistent with the proposal that the C_1 intermediates are methylenes, formed by probe decomposition under the conditions of the catalysis, which participate in the chain growth process.

Effect of ^{13}C-Labelled Probe Molecule Addition: General Considerations

When either the $^{13}CH_2N_2$ (Table 3A) or the $^{13}CH_3NO_2$ probe (Table 3B) was added to the $^{12}CO/H_2$ feedstream high levels of ^{13}C incorporation into the hydrocarbon products were found for all three catalysts. The data differed for the three metals investigated but showed trends which were self-consistent for any given catalyst.

The ^{13}C incorporation data were initially analysed on the premise that statistical mixing of the methylene units from syn gas and those from the probe molecules occurs. A binomial distribution function was used to calculate the expected levels of ^{13}C incorporation. The ratio of $^{12}C:{}^{13}C$ used in these experiments was ca. 9 : 1; thus undetectably low levels of products derived exclusively from the probe molecules, containing only ^{13}C, would be anticipated.

The results for the cobalt catalyzed reactions were close to those predicted. The most abundant peak was that for $^{12}C_n$ ($\equiv{}^{13}C_0$), and the amounts of $^{13}C_1$, $^{13}C_2$, $^{13}C_3, \ldots, {}^{13}C_n$, present in each C_n hydrocarbon decreased statistically, as expected for random mixing of labelled and unlabelled methylenes. Thus, for example, the 1-butene from addition of $^{13}CH_2N_2$ showed the following percentages: 66 ($^{13}C_0$), 18 ($^{13}C_1$), 10 ($^{13}C_2$), 2 ($^{13}C_3$), and 4 ($^{13}C_4$). The ^{13}C distribution of 1-butene found experimentally and the levels of ^{13}C incorporation calculated are also shown graphically in Fig. 4.

By contrast, the data obtained for reactions over rhodium were different and very unexpected: the isotope distribution in a C_n hydrocarbon fell from the maximum at $^{13}C_0$ via a trough at almost zero for intermediate ^{13}C values, *but peaked again* at $^{13}C_n$ (Tables 3A and 3B). Thus for example, the percentages for 1-butene from addition of $^{13}CH_2N_2$ were 69 ($^{13}C_0$), 3 ($^{13}C_1$), 0 ($^{13}C_2$), 1 ($^{13}C_3$), and 27 ($^{13}C_4$). The figures found when $^{13}CH_3NO_2$ was used as a probe were not dissimilar. These data can only be explained by postulating two quite separate paths for the formation of butene (and the other hydrocarbons), one from ^{12}CO, and the other from $^{13}CH_2N_2$ or $^{13}CH_3NO_2$. Since similar ^{13}C levels are obtained from both $^{13}CH_2N_2$ and $^{13}CH_3NO_2$, it would be anticipated that both probes should yield a common C_1 intermediate on the rhodium surface, which participates in chain growth. Thus it is puzzling why so little crossover occurs between the CO derived pathway and the probe derived pathway over rhodium; this question is further addressed below.

Experiments over ruthenium gave results intermediate between those found for cobalt and those for rhodium: hydrocarbon products were obtained which showed mixed ^{12}C and ^{13}C incorporation, as well as some that clearly arose from probe oligomerisation. Thus the 1-butene obtained from $^{13}CH_2N_2$ addition to the ^{12}CO stream contained 71% ($^{13}C_0$), 13% ($^{13}C_1$), 5% ($^{13}C_2$), 3% ($^{13}C_3$), and 8% ($^{13}C_4$).

One further feature of interest is that while the ^{13}C labelling of the ethene and the ethane showed a similar pattern to the labelling found for the higher hydrocarbons when $^{13}CH_3NO_2$ was the probe, that was not the case when $^{13}CH_2N_2$ was used as probe. There the *ethane* came very largely from the probe for all three metals (and contained $\geq$85% $^{13}C_2$). By contrast the *ethene* contained virtually no ^{13}C and was almost entirely $^{12}C_2H_4$ over Rh and Ru and largely so over Co. That would indicate that when $^{13}CH_2N_2$ was used as probe, formation of ethene and ethane follow independent routes and that the ethane does not arise from the ethene. One must conclude that there the ethene arises from the CO hydrogenation, while the ethane comes from the probe.

In addition to the hydrocarbons, some oxygenates (methanol, ethanol, and acetaldehyde) are produced in the CO hydrogenation, especially over Rh, but also to some extent over Ru and Co catalysts. However, ^{13}C incorporation from either $^{13}CH_2N_2$ or $^{13}CH_3NO_2$ was found to be significant only for methanol over Rh or Co; incorporation of ^{13}C from either probe into acetaldehyde or ethanol was very small over any of the three metals. This shows that the majority of the oxygenates arise directly from the carbon

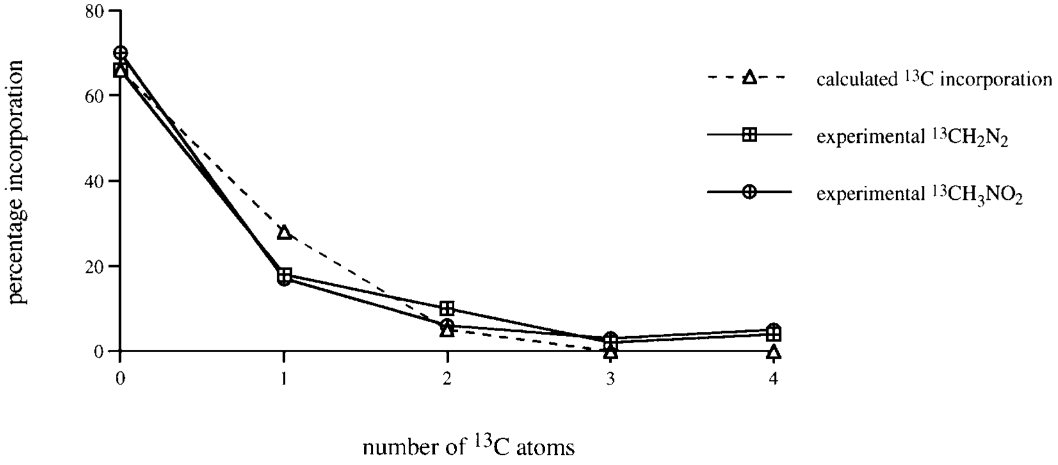

FIG. 4. Comparison between the calculated and the experimental levels of ^{13}C incorporation in 1-butene formed during addition of $^{13}CH_2N_2$ or $^{13}CH_3NO_2$ over Co/SiO$_2$ over Co/SiO$_2$ at 523 K.

monoxide hydrogenation and that the reactions leading to hydrocarbons and which are being probed proceed by different paths from those which lead to oxygenates. The lack of incorporation of ^{13}C into oxygenates when $^{13}C_2H_3Br$ or $^{13}C_2H_4$ were used as probes for CO hydrogenation reactions has already been noted (9) and led to a similar conclusion.

Reactions of Diazomethane Probes

No nitrogen-containing compounds were detected among the products when CH_2N_2/H_2 mixtures, with or without added CO, were passed over any of the Rh, Ru, or Co catalysts studied. In the absence of CO, the main products formed were methane by probe hydrogenation, ethane, and small amounts of higher alkanes. In the presence of CO, a product distribution characteristic of that produced by the Fischer–Tropsch reaction was obtained.

The uncatalysed gas phase decomposition of diazomethane has been reported by other workers to produce mainly CH_4, C_2H_6, C_2H_4, and C_2H_2; in the presence of excess H_2, only CH_4 and C_2H_6 were produced (19). Surfaces and some metals (e.g., Cu and Au) do promote the decomposition of diazomethane to polymethylene.

Reactions of Nitromethane Probes and Amine Formation

Nitromethane decomposed completely when passed over any of the three catalysts under our normal conditions and was not detected among the products. The reaction of CH_3NO_2 with hydrogen (either in the presence or the absence of CO) over rhodium and ruthenium gave small amounts of trimethylamine and some acetonitrile, Me_2NEt, and traces of $MeNEt_2$ (Tabel 4). That was in addition to the usual Fischer–Tropsch products, when CO was present. Very small amounts of nitrogen-containing products were formed over the cobalt catalyst.

No primary or secondary amines were detected in any of the reactions. Low selectivity towards primary amines has also been seen previously in the reactions of syn gas and olefins in the presence of NH_3 (20). We have confirmed that and have shown that when ammonia is pulsed into a stream of syn gas over rhodium under Fischer–Tropsch conditions, acetonitrile, trimethylamine, and dimethylamine were formed (approximately equal ratios). A very similar result was found when methylamine was used as probe.

TABLE 4

N-Containing Products Formed (μmol/gcat/h) during Addition of $^{13}CH_3NO_2$ to Syn Gas Feed Stream over Rhodium, Ruthenium and Cobalt Catalysts at 523 K

Product	Catalyst Rh/Ce/SiO$_2$	Ru/SiO$_2$	Co/SiO$_2$
Trimethylamine	7	3	0.01
Acetonitrile	1	1	—
Dimethylethylamine	1	0.4	—
Diethylemethylamine	0.1	0.2	—
Propionitrile	Trace	—	—

Note. —, not detected.

The reorganisation of primary to secondary and tertiary amines over metals has been discussed by Roundhill (21); the alkyl exchange reactions of tertiary amines (22) and the dehydrogenation of primary amines to nitriles (23) induced by metals have also been reported. It is likely that all these processes occur in our reactions and that the formation of trimethylamine and acetonitrile in the reactions involving nitromethane proceeds via methylamine.

When the nitrogen-containing compounds obtained from a $^{13}CH_3NO_2$ probe were analysed, it was found that 60% of the Me_3N obtained over rhodium and 97% of the Me_3N obtained over ruthenium contained either $^{13}C_3$ or $^{13}C_2$; similarly most (90% over Rh, 78% over Ru) of the MeCN formed contains $^{13}C_2$. This indicates that the carbons derive mainly from the $MeNO_2$ probe molecule; the coexistence of ^{13}C and of N in these two compounds suggests that they retain the C–N bond of probe. Our labelling studies thus indicate that it is likely that the trimethylamine formed over rhodium is derived to the extent of ca. 60% from $^{13}CH_3NO_2$ via $^{13}CH_3NH_2$. The remaining ca. 40% trimethylamine must then be derived from the syn gas reaction over rhodium (possibly from $^{12}CH_3OH$) and ammonia. Amine formation involving syn gas appears to be a very minor path over ruthenium; that would be consistent with ruthenium being much poorer at forming methanol and other oxygenates than is rhodium under Fischer–Tropsch conditions.

Two Methylene Growth Reactions

Our data showing that addition of $^{13}CH_2N_2$ or $^{13}CH_3NO_2$ probes to the ^{12}CO hydrogenation over rhodium results in the formation of the unexpected fully $^{13}C_n$ as well as the expected fully $^{12}C_n$ labelled hydrocarbon products means that here the reactive C_1 species derived from the probe molecule on the surface is not interchangeable with the C_1 species from $CO + H_2$ on the surface. It implies the coexistence of two CH_2 oligomerisation mechanisms. While it is perhaps just about conceivable that the same species is formed in each case but in two different sites on the surface, thus making exchange and crossover impossible, we prefer to consider a more chemically significant explanation. That would imply that the species from $CO + H_2$ is different from that derived from the probe, at least over rhodium. There now exists a great deal of evidence which supports surface methylene as an intermediate in CO hydrogenation (5, 6, 13–15). If we accept that this is so, our results imply that a polymethylene oligomer can be formed from the probe by a path that does *not* proceed via a surface methylene, but via some other C_1 intermediate, (A). However the methylene and the other intermediate species (A) are clearly linked in some way, since over cobalt there is essentially complete scrambling of label between labelled probe and unlabelled CO, suggesting that there the same surface methylene is formed from both.

Our data thus suggest that two paths are available for polymethylene formation from the probe; one, over cobalt, goes via complete probe decomposition to methylene which can then scramble freely and randomly with methylene from $CO + H_2$. However, over rhodium the data imply that there is a second possibility, namely that decomposition of both diazomethane and nitromethane is a two-step process, via a surface species (A), different from, but related to, methylene. It is most likely to be a precursor to methylene and thus one may presume that it is formed in all the probe decompositions.

Thus (A) can then react in two ways:

(i) It can undergo a homo-oligomerisation with other (A) to give α-olefins, by a path which is separate and distinct from the normal carbon monoxide-derived homo-oligomerisation and where (A) does not react via surface methylenes, but in some other way. This occurs over rhodium.

(ii) Alternatively (A) can give a methylene surface species that is now identical to that from CO hydrogenation, and which can then interact randomly with other surface CH_2 species. This occurs over cobalt, where presumably (A) has a very short lifetime, too short to oligomerise as in (i) above.

Further experiments will be needed to shed more light on the identity of (A). One possibility is that it still retains the C–N bond of probe, for example as CH_2N_2–(surface) or $CH_2{=}N$–(surface). A possible pathway for a diazomethane-derived polymethylene oligomerisation over rhodium might therefore proceed as follows:

$$CH_2{=}NN\text{–surface} + CH_2{=}NN\text{–surface} \rightarrow N_2\text{–}CH_2CH_2\text{–}N_2\text{–surface}$$

$$N_2\text{–}CH_2CH_2\text{–}N_2\text{–surface} + nCH_2{=}NN\text{–surface} \rightarrow N_2\text{–}CH_2(CH_2)_nCH_2\text{–}N_2\text{–surface} + N_2$$

$$N_2\text{–}CH_2(CH_2)_nCH_2\text{–}N_2\text{–surface} \rightarrow CH_2{=}CH(CH_2)_{n-1}CH_3 + nN_2 + \text{surface}.$$

Since over rhodium diazomethane and nitromethane behave very similarly, an analogous path can also be envisaged for the latter probe. The fact that amines are found only from the reactions involving nitromethane suggests that (A) may not be directly involved in amine formation, but that they arise from methylamine formed directly by hydrogenation of a surface nitromethane. This proposal is given some support by recent work on reactions of diazomethane metal complexes. Hidai and Ishii have shown (24) that stoichiometric C–C bond formation without cleavage of the C–N bonds occurs in the electroreduction of the diazomethane–tungsten complex, *trans*-$[WF(NNCH_2)(dppe)_2]BF_4$ to give $[(dppe)_2WF(N{=}NCH_2CH_2N{=}N)WF(dppe)_2]$. Somewhat related C–C couplings without C–N cleavage were also found in some oxidative couplings too. Although no oligomerisation products were found in these reactions, that is not surprising since tungsten is not a Fischer–Tropsch active metal and generally participates in oligo- or polymerisations via carbene plus olefin metathesis reactions.

Surface studies by Solymosi and his collaborators (25) have also shown that CH_2 (derived from CH_2I_2) on Rh(111) was stable up to 300 K, when it decomposed, largely to methane; only traces of ethene were found. By contrast, CH_2 (from CH_2Cl_2) on Pd(100) dimerised to ethene above 263 K. These results imply that methylene on rhodium is rather stable and that there is no strong tendency to create C–C bonds by $CH_2 + CH_2$ dimerisation. This result very much supports our own conclusions about the intimate mechanism of C–C coupling involving methylenes in carbon monoxide hydrogenation over rhodium (and other Fischer–Tropsch active metals), but which were based on studies involving model dirhodium complexes (7, 9, 10).

A solution reaction of a defined metal complex very relevant to our heterogeneous catalytic investigations is that of diazomethane with $[Rh(CO)(\mu\text{-dppm})_2Os(CO)_3]^+$ to give the η^1-allyl complex, $[CH_2{=}CHCH_2Rh(\mu\text{-dppm})_2Os(CO)_3Me]^+$ (26). Although no mechanistic details are known, it is evident that a $C + C + C$ coupling must occur to give the η^1-allyl ligand.

Over cobalt the probes decompose to surface methylenes. The results of ^{13}C labelling experiments are consistent with levels of ^{13}C incorporation based on the statistical mixing of $^{12}CH_2$ and $^{13}CH_2$ units; the data are also consistent with the hypothesis put forward earlier where chain propagation occurs by reaction of surface methylenes with surface alkenyl groups. The labelling studies indicate that the situation over ruthenium is intermediate between that over cobalt and that over rhodium.

SUMMARY

Addition of CH_2N_2 or CH_3NO_2 probes during CO hydrogenation over a cobalt on silica catalyst led to the incorporation of probe-derived methylenes into the hydrocarbon products. That both CH_2N_2 and CH_3NO_2 are effective C_1 precursors is supported by the observation that both probes enhance both the rate and the chain growth probability. Labelling studies using $^{13}CH_2N_2$ or $^{13}CH_3NO_2$ show that the $^{13}CH_2$ intermediates react with chemically indistinguishable surface $^{12}CH_2$ groups formed from $^{12}CO/H_2$ leading to random incorporation into the reaction products. Our new results offer strong support to the original Fischer–Tropsch hypothesis of the involvement of methylenes in carbon monoxide hydrogenation, and are also consistent

with levels of ^{13}C incorporation expected for the reactions of statistically mixed $^{12}CH_2$ and $^{13}CH_2$ units with surface alkenyl groups, as proposed in our alkenyl cycle hypothesis (9, 10).

By contrast, similar experiments over rhodium catalysts give parallel chain growth reactions each of which leads to the formation of hydrocarbons. One is CO hydrogenation which gives products derived exclusively from ^{12}C, the other is a homo-oligomerisation of probe derived methylene intermediates giving fully ^{13}C-labelled hydrocarbons. We suggest that the latter products arise from the probe by a path not involving surface methylenes, but in which surface CH_2N_2 or surface CH_3NO_2 undergo C–C bond formation befsre cleavage of the C–N bonds; some mechanistic suggestions are made.

In addition to the products of CO hydrogenation, rhodium promotes a selective reaction when CH_3NO_2 is added to the CO/H_2 feed stream leading to the formation of significant amounts of trimethylamine and acetonitrile. These results suggest incomplete decomposition of the probe over rhodium with retention of the C–N bond.

The same probe experiments over ruthenium gave results intermediate between those found for cobalt and rhodium.

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26. Cowie, M., and Sterenberg, B., personal communication.