JOURNAL OF CATALYSIS 141, 355–367 (1993)

In Situ FTIR Study of CO/H_2 Reactions over Ru/SiO_2 at High Pressure and Temperature

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Received September 25, 1992; revised January 15, 1993

Infrared spectra are reported of Ru/SiO_2 at 473, 503 or 553 K and exposed to CO/H_2 mixtures at 3, 15, or 30 bar and $CO:H_2$ ratios of 14 : 1, 1 : 2, and 1 : 14. A band due to linearly adsorbed CO, which shifted to lower wavenumbers with increasing temperature and was both shifted and weakened with increasing time, was influenced by the dissociative adsorption of CO, structural reorganisation and sintering of Ru, and the build-up of surface hydrocarbon *in situ* during reaction. Both linear RuCO and a μ-bonded Ru carbonyl were precursors of active intermediates in reactions leading to methane and higher hydrocarbon products. Three types of surface hydrocarbon were present *in situ* during reaction: these were ethoxy groups on the silica support, probably derived from reaction of ethene with silanol groups, methylene chains (with methyl end groups) possibly bonded to Ru via a single CH_2 end group, and CH_2 groups specifically bonded to Ru. The formation of methylene-containing adsorbed species was favoured by increasing pressure, but the effect of temperature depended on the total reaction pressure. Increasing the $CO:H_2$ ratio favoured C–C chain growth. The infrared results support the proposal that hydrocarbonaceous species may be further hydrogenated on the Ru surface to give methane.

INTRODUCTION

The formation of methane over ruthenium catalysts is believed to involve dissociative adsorption of CO to give adsorbed carbon which subsequently reacts with hydrogen (*1–3*). Carbon monoxide is also nondissociatively adsorbed on ruthenium and gives infrared bands which have been attributed to linear carbonyl (RuCO) or gem-dicarbonyl ($Ru(CO)_2$) complexes of Ru at either reduced or oxidised surface sites (*4–6*). The band position for RuCO is influenced by surface coverage (*7*) or by the simultaneous presence of hydrogen in contact with the metal surface (*8*). There have been several *in situ* studies of supported ruthenium in CO/H_2 mixtures at elevated temperatures (*6, 8–12*). A distinction has been identified between the reactivity of $Ru(CO)_2$ and RuCO species with hydrogen (*6*), and spectra in the ν_{CH} region generally show dominant bands due to adsorbed species containing methylene groups. However, product species from CO/H_2 over transition metal catalysts depend on a variety of system variables including CO/H_2 ratio and pressure (*13*), and therefore the present work was aimed at identifying surface species on Ru in Ru/SiO_2 catalysts exposed to CO/H_2 at different CO/H_2 ratios, high temperature, and high total pressures which differed by an order of magnitude.

EXPERIMENTAL

A homogeneous paste prepared from Grace grade 432 silica and aqueous ruthenium nitrosyl nitrate (Johnson Matthey) was dried in air (383 K, 16 h) before being compressed (7 ton on die) into self-supporting discs (100 mg weight, 25 mm diameter). A disc mounted in a stainless steel high pressure (<175 bar) infrared cell fitted with fluorite windows was raised to 773 K in a flow (200 cm^3 min^{-1}, 0.1 MN m^{-2}) of 3.5% hydrogen in argon and held at 773 K for 1 h before evacuation (773 K, 30 min) and cooling to reaction temperature ($295 < T/K \leq 553$). Spectra of discs *in situ* in CO, CO/H_2, CO/CH_4, or a flow of argon saturated with methanol or ethanol at the

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quoted temperatures and pressures were recorded at 4 cm^{-1} resolution with a Perkin–Elmer 1750 FTIR spectrometer.

The silica support was totally amorphous with a surface area of 320 ± 6 $m^2 g^{-1}$ (BET, N_2, 77 K), a total pore volume (<50 nm) of 1.12 ± 0.01 $cm^3 g^{-1}$, and a mean pore diameter of 14 nm. After impregnation and reduction the corresponding figures for Ru/SiO_2 catalyst were 296 ± 6 $m^2 g^{-1}$, 1.04 ± 0.01 $cm^3 g^{-1}$, and 14 nm. XRF showed that the reduced catalyst contained 2.0 wt% Ru. Hydrogen chemisorption gave an uptake of 0.81 cm^3 (g catalyst)$^{-1}$ at STP which corresponds to a H : Ru ratio of 0.37 : 1 or 37% dispersion.

RESULTS

Adsorbed CO and Alcohols

Spectra of reduced Ru/SiO_2 were subtracted from spectra recorded after exposure of a catalyst disc to CO at 5 atm. In the resulting difference spectra possible bands above 2080 cm^{-1} due to adsorbed CO (*4*, *5*) were obscured by the intense band envelopes at 2120 and 2170 cm^{-1} due to CO gas. In accordance with previous observations (*5*, *7–9*, *11*, *12*) the dominant band for catalyst at 295 K was at 2049 cm^{-1} and may be attributed (*4*) to linearly adsorbed CO on ruthenium sites in the zero oxidation state. As the temperature was gradually raised to 723 K, the band narrowed and shifted to 2026 cm^{-1} with only a slight change in intensity. The band reverted to its original position when the disc was cooled in CO to 295 K. A weak, broad band also appeared in the spectra at 1750–1800 cm^{-1}.

Spectra of Ru/SiO_2 in CO(5 atm)/H_2(10 atm) for short times (<*ca.* 1 h) exhibited a maximum at ca. 2049 cm^{-1} at moderate temperatures (295–573 K), the maximum shifting towards ca. 2026 cm^{-1} at high temperatures (> 623 K). However, an additional band also appeared at 2010 cm^{-1} when the temperature was above 523 K. The latter band remained in the spectrum when the sample was cooled to ambient temperature and may result from coadsorption of CO and H-adatoms at exposed Ru sites (*14*).

Syngas catalysis over Ru/SiO_2 generally favours alkanes and alkenes as products (*15*), although in homogeneous systems catalysis by ruthenium complexes can lead to significant amounts of methanol and ethanol (*16*). Spectra of Ru/SiO_2 exposed to alcohols at 473 K were therefore recorded in order that the products of adsorption could be recognised if they were also formed from CO/H_2 over Ru/SiO_2. Spectra in the ν_{CH} and δ_{CH} regions were dominated by bands due to alkoxy groups on the silica support. As for silica alone (*17*), the bands were at 2958, 2857, 1481/1464, and 1374 cm^{-1} for SiOMe groups and at 2981, 2938, 2906, 1457, and 1397 cm^{-1} for SiOEt groups. Bands due to surface complexes of ruthenium, if present, were obscured by the maxima due to SiOMe or SiOEt groups, except for narrow bands at 2018 cm^{-1} and 2010 cm^{-1} due to linear RuCO formed from methanol and ethanol, respectively. Both alcohols also gave a weak broad maximum at 1750–1800 cm^{-1}.

CO/H_2 Reactions (3 bar)

Figure 1 shows spectra of Ru/SiO_2 (minus the spectrum before the addition of gases) exposed to a 1 : 2 ratio of CO : H_2 at a total pressure of 3 bar and at 553 K. A strong band at 2031 cm^{-1} due to linear RuCO species immediately appeared (Fig. 1(a)] but decreased in intensity and shifted to 2017 cm^{-1} as a function of time [Fig. 1(h)]. After 25 h reaction the CO(g) in the system had been completely used up as shown by the disappearance of the *P*- and *R*-branch band envelopes at 2120 and 2170 cm^{-1} [Fig. 1(h)]. The most intense band at 3016 cm^{-1} in the product spectra was due to methane gas and was accompanied by *P* and R branches exhibiting rotational fine structure. The loss of CO(g) resulted in subsequent loss of the maximum at 2017 cm^{-1} [Fig. 1(i)] which was accompanied by continued growth of the band at 3016 cm^{-1} due to CH_4(g), suggesting that RhCO was in-

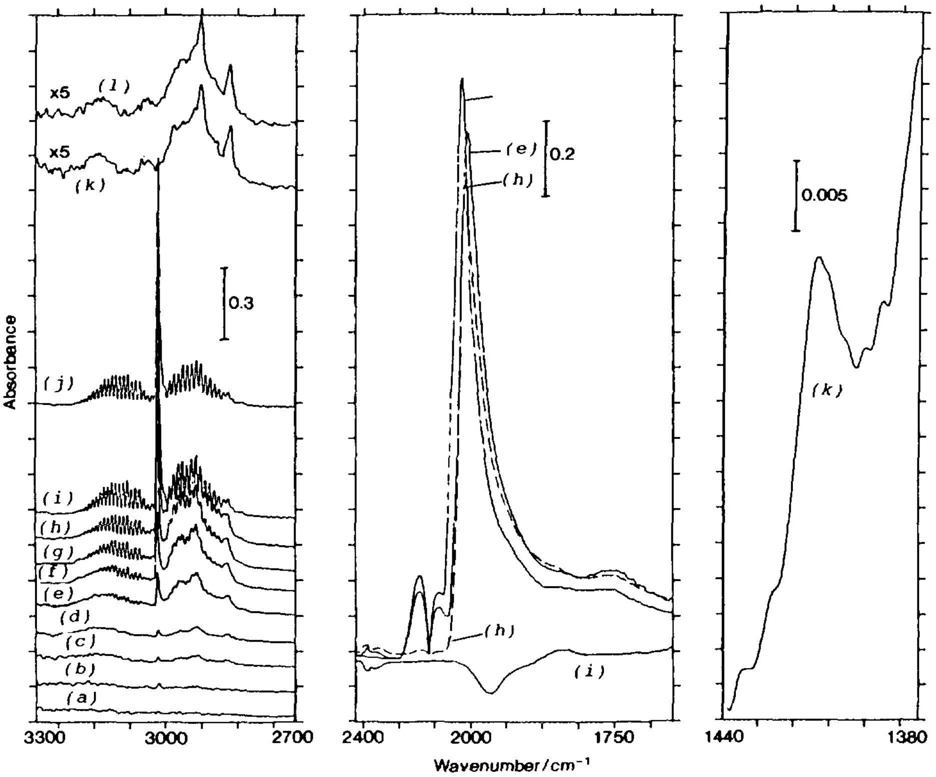

FIG. 1. Spectra of Ru/SiO_2 exposed to CO (0.1 MN m^{-2})/H_2(0.2 MN m^{-2}) at 553 K for (a) ca. 10 s, (b) 5 min, (c) 30 min, and (d) 1, (e) 5, (f) 10, (g) 20, (h) 25, (i) 26, and (j) 45 h, and after subsequent evacuation at (k) 553 K (10 min), and (l) 723 K (10 min).

volved as an intermediate in the formation of methane. A weak band at ca. 1750 cm^{-1} in spectra of Ru/SiO_2 exposed to CO/H_2 [Fig. 1] also disappeared after the CO(g) present had completely reacted suggesting that a further form of adsorbed CO on Ru, possibly a bridged species (*4*) was present. A similar band appeared in spectra of Ru/SiO_2 exposed to CO alone at 5 bar or to methanol or ethanol at 473 K.

There was no further increase in the intensity of bands due to CH_4(g) after both CO(g) and adsorbed CO complexes (2017 and 1750 cm^{-1}) had been removed by reaction [Fig. 1(j)].

The *P* branch of the CH_4(g) spectrum obscured coincident bands due to adsorbed products of reaction. The intensities of the coincident bands increased with time while CO(g) was present [Fig. 1(a)–(g)] but decreased in intensity at the same time as adsorbed CO underwent reaction [Fig. 1(h), (i)] before attaining a stable level of absorbance [Fig. 1(i), (j)]. Removal of methane by evacuation at 553 K revealed bands at 2981, 2917, and 2851 cm^{-1}, together with a weaker band at 1410 cm^{-1} in the lower spectral region [Fig. 1(k)]. Raising the temperature to 723 K [Fig. 1(l)] had negligible effect on the bands at 2917 and 2851 cm^{-1}, although the weaker band at 2981 cm^{-1} was further weakened revealing an additional shoulder at 2935 cm^{-1}. A weak maximum at 3153 cm^{-1} may have been indicative of an adsorbed unsaturated hydrocarbon species present after reaction.

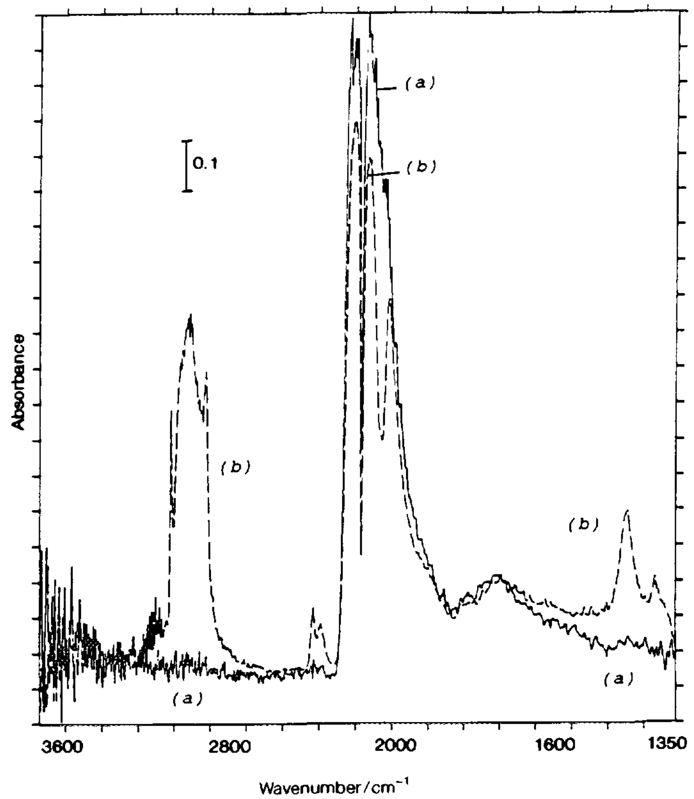

FIG. 2. Spectra of Ru/SiO$_2$ exposed to CO (1.0 MN m^{-2})/H$_2$(2.0 MN m^{-2}) at 553 K for (a) ca. 10 s and (b) 65 h.

CO/H$_2$ Reactions (30 *bar*)

Increasing the total initial reactant pressure to 30 bar retaining a 1 : 2 ratio of CO : H$_2$ gave significantly different relative selectivities to methane gas and adsorbed hydrocarbon products than those observed for a 3-bar reaction mixture. Results for reactions at 30 bar and 503 or 553 K were similar in selectivity terms for adsorbed products, although at the higher temperature all the products were generated much more quickly and there was also a higher selectivity towards the formation of methane. Figure 2 shows the immediate and long-term spectrum of Ru/SiO$_2$ exposed to CO/H$_2$ (30 bar) at 553 K. The reaction of CO(g) led to decreases in intensity of the band envelopes at 2170 and 2120 cm^{-1} which led to a shoulder at ca. 2030 cm^{-1} developing into a distinct weaker band at 2017 cm^{-1} due to ruthenium linear carbonyl. The band at 1750 cm^{-1}, possibly due to a bridged carbonyl of ruthenium, was unchanged during reaction. Methane (3016 cm^{-1}) appeared more rapidly from CO/H$_2$ initially at 3 bar rather than 30 bar, but considerably more adsorbed hydrocarbon was generated at the higher pressure. The latter is more clearly revealed by spectra recorded after removal of the gas phase by evacuation [Fig. 3(a), (b)]. The high pressure experiment gave a multiplicity of bands in the ν_{CH} region. Bands at 2970, 2947, 2897, 2880, and 2860 cm^{-1} were addi-

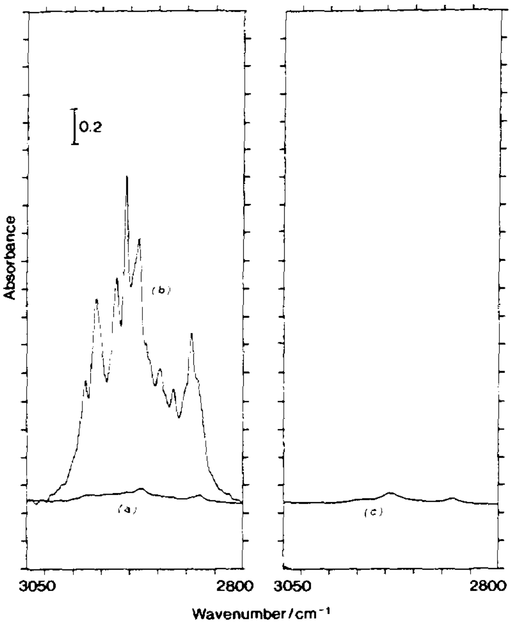

FIG. 3. Spectra of Ru/SiO_2 evacuated at 553 K after exposure at 553 K to (a) CO (0.1 MN m^{-2})/H_2 (0.2 MN m^{-2}) for 45 or 65 h, (b) CO (1.0 MN m^{-2})/H_2 (2.0 MN m^{-2}) for 65 h, and (c) CO (0.2 MN m^{-2})/CH_4 (0.1 MN m^{-2}) for 70 h.

tional to maxima at 2981, 2935, 2917, and 2851 (sh) cm^{-1} also observed after reaction at lower pressure. Maxima also appeared in the δ_{CH} spectral region at 1460 and 1395 cm^{-1} [Fig. 2(b)]. A doublet at ca. 2350 cm^{-1} [Fig. 2(b)] showed that a trace of gaseous carbon dioxide was formed during reaction.

The generation of methane as a significant product from CO/H_2 at high pressure led to an experiment which tested whether CH_4/CO mixtures underwent any secondary reactions giving adsorbed species. The result of one typical experiment is compared on the same absorbance scale in Fig. 3 with results for CO/H_2 mixtures at 3 and 30 bar. Weak maxima at 2926 and 2854 cm^{-1} [Fig. 3(c)] resembled bands at 2917 and 2851 cm^{-1} for CO/H_2 at 3 bar [Fig. 3(b)] but contrasted, not only in band positions but also in intensities, with the band envelope for Ru/SiO_2 exposed to CO/H_2 at 30 atm [Fig. 3(b)].

CO/H_2 Reactions (15 *bar*)

A hydrogen-rich CO/H_2 mixture reacted over Ru/SiO_2 at 473 K to give little methane (3016 cm^{-1}) but generated adsorbed hydrocarbon groups with infrared bands at 2963, 2931, and 2857 cm^{-1} [Fig. 4] and ca. 1460 cm^{-1}. Reaction at 503 K gave a more intense band at 3016 cm^{-1} due to methane [Fig. 5] and reaction at 553 K gave spectra in the ν_{CH} region in which bands due to methane were dominant [Fig. 6]. Bands due to adsorbed hydrocarbon were revealed by evacuation [Fig. 6(b)] and are compared in Fig. 6 with the corresponding bands appearing after reaction at 473 and 503 K. The generation of adsorbed hydrocarbon groups was faster at 503 K than 473 K, the resulting spectra being similar with respect to maxima at ca. 2960, 2931, and 2857 cm^{-1}

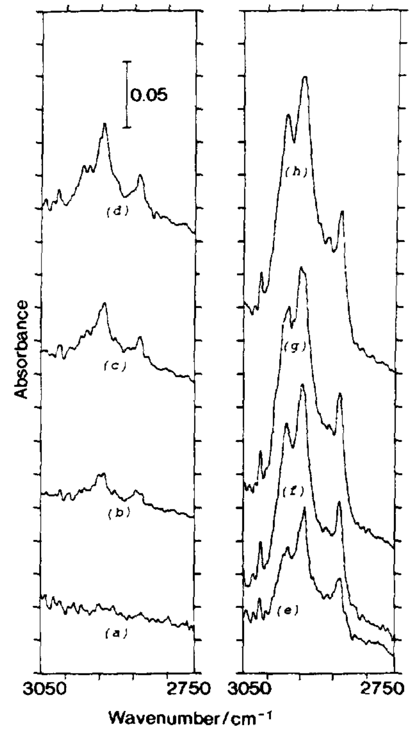

FIG. 4. Spectra of Ru/SiO_2 exposed to CO (0.1 MN m^{-2})/H_2 (1.4 MN m^{-2}) at 473 K for (a) *ca.* 10 s and (b) 1, (c) 5, (d) 10, (e) 20, (f) 50, (g) 60, and (h) 67 h.

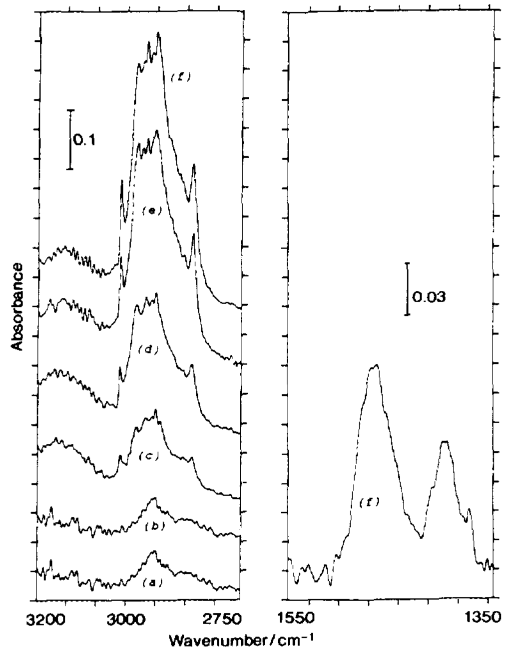

FIG. 5. Spectra of Ru/SiO$_2$ exposed to CO (0.1 MN m^{-2})/H$_2$ (1.4 MN m^{-2}) at 503 K for (a) ca. 10 s and (b) 1, (c) 10, (d) 20, (e) 50, and (f) 72 h.

but differing in that an additional band appeared at 2981 cm^{-1} after reaction at 503 K [Fig. 6(c)]. The hydrocarbon species responsible for these bands were not desorbed by evacuation even when the temperature was raised to 723 K. Bands at 1465 and 1395 cm^{-1} due to CH deformation vibrations were particularly well developed after reaction at 503 K [Fig. 5(f)]. The ν_{CH} band envelope after reaction at 553 K and evacuation at 553 K to remove methane was very weak [Fig. 6(b)] and hence showed a poor signal-to-noise ratio, but exhibited the same maxima in similar relative proportions to the result for reaction at 503 K.

The spectroscopic effects in the ν_{CO} region for Ru/SiO$_2$ exposed to CO/H$_2$ at 15 bar and a 1 : 14 ratio were similar to the corresponding effects for a 1 : 2 ratio at 3 bar [Fig. 1] and 30 bar [Fig. 2]. The complete depletion of CO(g) to zero after 41 h reaction at 553 K led to the rapid disappearance of the maxima at 2017 and 1760 cm^{-1} due to adsorbed CO on ruthenium.

For a 1 : 2 ratio of CO : H$_2$ at 15 bar and 503 K, bands in the ν_{CH} region due to adsorbed species grew with time at 2960(sh), 2931, and 2857 cm^{-1} with the concomitant growth of two maxima at 1465 and 1395 cm^{-1} [Fig. 7A]. The rate of formation of methane (3016 cm^{-1}), slow at 503 K [Fig. 7A], was ca. 3.5 times faster at 553 K [Fig. 7B], bands in the P-branch envelope for methane partially obscuring ν_{CH} bands due to adsorbed species. The latter were revealed at 2966, 2935, 2900(sh), and 2860 cm^{-1} after evacuation at 553 K [Fig. 7(j)] and were accompanied by bands at 1465 and 1395 cm^{-1} [Fig. 7(h)]. The rate of growth of maxima due to adsorbed CH-containing groups at 553 K was intermediate between the corresponding rates for 1 : 2 ratios of CO : H$_2$ at initial pressures of 3 and 30 bar [Fig. 3], the rate becoming faster with increasing pressure. In contrast, the rate of methane formation decreased with increasing total pressure at 553 K. Furthermore, the rate of methane formation at 553 K was less for a 1 : 2 ratio of CO : H$_2$ than for a 1 : 14 ratio [Fig. 6(a)] at a fixed initial total pressure of 15 bar. However, more adsorbed hydrocarbon was generated with the 1 : 2 ratio [Fig. 6] than with the 1 : 14 ratio [Fig. 7(i), (j)] at both 503 and 553 K. For both CO/H$_2$ ratios there were less adsorbed CH-species present *in situ* during reaction at 553 K than at 503 K. The simple explanation that the adsorbed species were more readily desorbed at the higher temperature is not tenable because the infrared band intensities were unaffected by subsequent evacuation of catalyst up to 723 K.

No methane was formed from a 14 : 1 mixture of CO : H$_2$. Bands at 2931 and 2857 cm^{-1} due to adsorbed hydrocarbon were extremely weak even after prolonged reaction at 503 or 553 K [Fig. 8]. The maximum due to RuCO was obscured by intense maxima due to gas-phase CO and could not therefore be monitored. A weak doublet

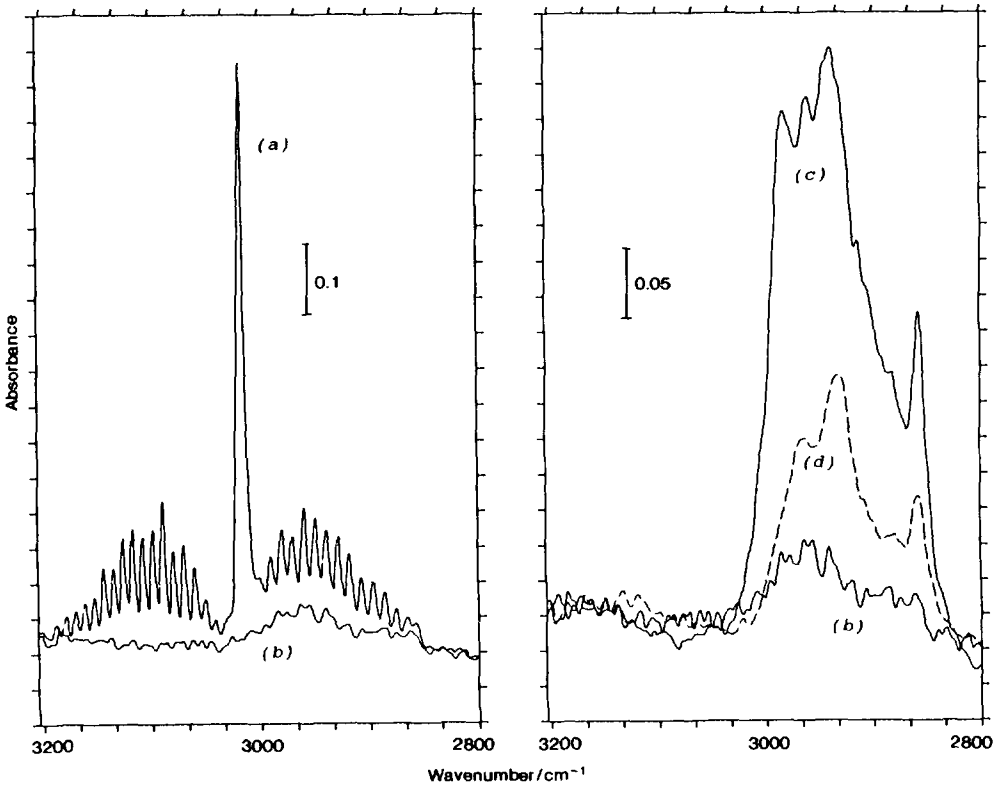

FIG. 6. Spectra of Ru/SiO_2 exposed to CO (0.1 MN m^{-2})/H_2 (1.4 MN m^{-2}) (a) for 40 h at 553 K, (b) after subsequent evacuation at 553 K, (c) for 72 h at 503 K followed by evacuation at 503 K, and (d) for 67 h at 473 K followed by evacuation at 473 K.

growing at 2350 cm^{-1} suggested that some carbon dioxide was formed in the system.

In accordance with a previous observation (14), no infrared bands due to adsorbed formate were observed for Ru/SiO_2 in CO/H_2 at high temperature.

DISCUSSION

Surface Carbonyl Complexes

Weak bands at ca. 2080 and 2145 cm^{-1} for CO at low pressure on Ru/SiO_2 have been ascribed to a $Ru^{n+}(CO)_2$ complex (5, *11*). However, if these bands existed in the present spectra, they were obscured by intense band envelopes due to CO(g). The bands could not be revealed by removal of CO(g) because the $Ru^{n+}(CO)_2$ complex on Ru/SiO_2 is unstable to evacuation (*11*). The weak adsorption of CO at sites leading to the $Ru^{n+}(CO)_2$ complex also implies that at elevated temperatures there would only be at most low coverage of the available surface sites (*11*).

The infrared band position for linearly adsorbed CO on Ru(001) shifted towards lower wavenumbers with decreasing surface coverage (*7*). Similarly a shift from 2030 to 2010 cm^{-1} accompanied the partial desorption of CO from Ru/SiO_2 by evacuation at 373 K (*5*). The present shift from 2049 to 2026 cm^{-1} which occurred with increasing temperature from 295 to 723 K cannot be attributed to decreasing surface coverage because, with 5 bar of CO(g)

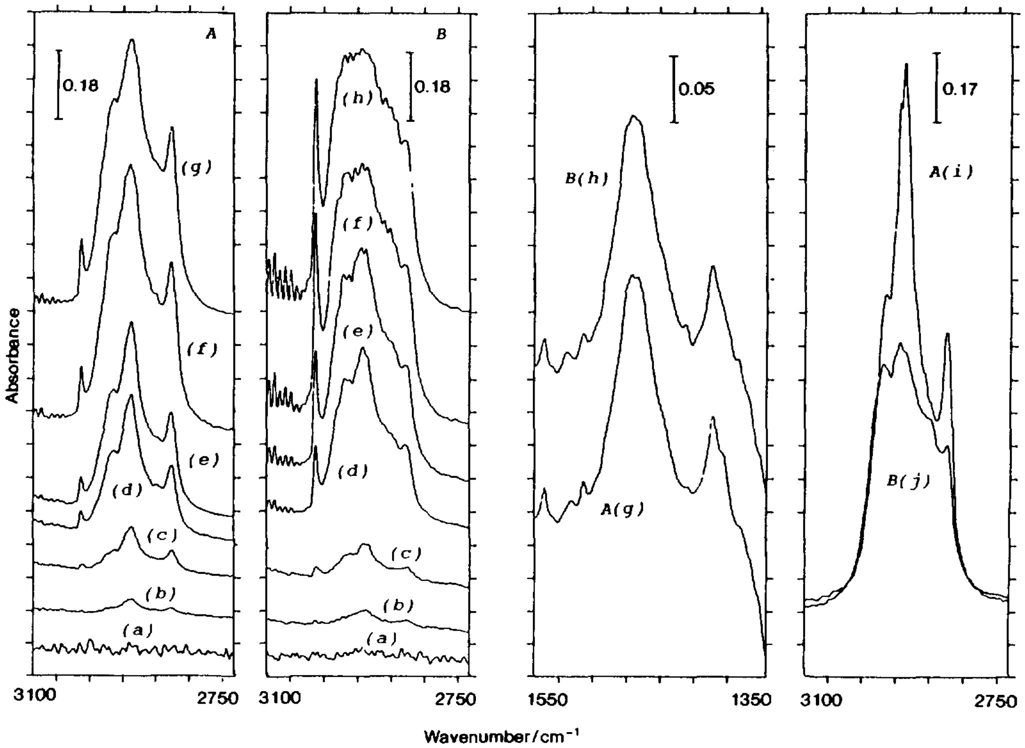

FIG. 7. Spectra of Ru/SiO$_2$ exposed to CO (0.5 MN m^{-2})/H$_2$ (1.0 MN m^{-2}) at (A) 503 K and (B) 553 K for (a) ca. 10 s, (b) 5 min, and (c) 1, (d) 10, (e) 20, (f) 50, (g) 65, and (h) 70 h, followed by subsequent evacuation at (i) 503 K and (j) 553 K.

present, the band shift was only accompanied by a slight reduction in band intensity. Coverage of surface sites was high even at 723 K. One explanation would be that increasing dissociative adsorption of CO with increasing temperature at sites other than those giving RuCO releases oxygen to the ruthenium surface and therefore lowers ν_{CO} for the linear surface RuCO complex (*11*, *18*). However, the return of the band to 2049 cm^{-1} on cooling in CO to 295 K is difficult to rationalise if the adatoms resulting from dissociative adsorption were retained on the surface during the cooling process. An alternative factor contributing to the band shifts would be structural reorganisation of the ruthenium with changing temperature in the presence of carbon monoxide.

The interaction of carbon monoxide with oxide-supported ruthenium may lead either, at low temperatures, to oxidative disruption of Ru–Ru bonds to give adsorbed Ru^{n+}(CO)$_x$ complexes ($x \geq 2$) (*19–22*) or, at high temperatures, to reductive agglomeration of Ru^{n+} species to Ru^0 clusters (*19*, *22*). However, the extent of these effects is strongly influenced by the nature of the oxide support (*21*). Oxidative disruption is clearly observed for Ru/Al$_2$O$_3$ (*19*, *21*, *22*) and has led to the appearance of infrared bands at 2075 and 2140 cm^{-1} which were attributed to a Ru^{n+}(CO)$_2$ species (n = 1–3) (*19*). The failure to observe such bands here after contact between CO and Ru/SiO$_2$ at 295 K suggests that oxidative disruption cannot have occurred to any significant extent. This is substantiated by the present

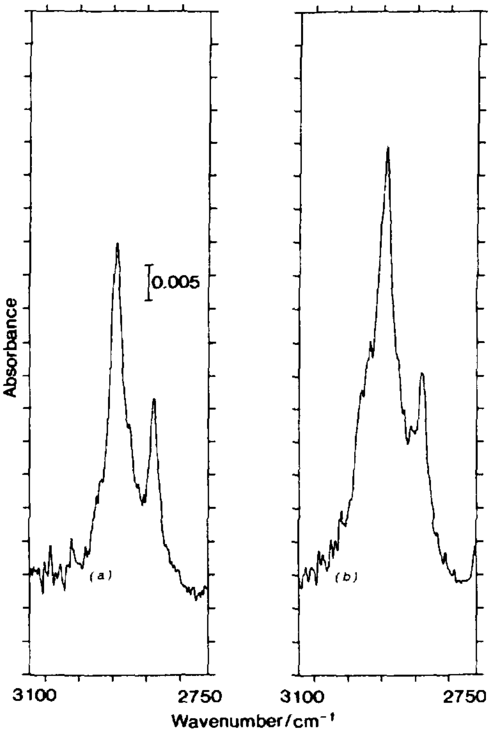

FIG. 8. Spectra of Ru/SiO_2 exposed to CO (1.4 MN m^{-2})/H_2 (0.1 MN m^{-2}) for (a) 65 h at 503 K and (b) 90 h at 553 K.

dominant infrared band positions for CO on Ru/SiO_2 at 295–723 K which were typical of CO complexes of Ru in the zero oxidation state. This conclusion supports a previous report (*21*) that oxidative disruption of Ru–Ru bonds by CO does not occur for Ru/SiO_2. The present band shifts on raising the temperature cannot therefore be attributed to changing Ru oxidation state but may be influenced by agglomeration of Ru^0 particles, this process possibly being affected by the presence of hydrogen (19).

Bridging carbonyl species on ruthenium are not often observed (*4*, *5*). Yamasaki *et al.* (*11*) recorded a broad band at 1700–1900 cm^{-1} which was assigned to Ru_2CO species for Ru/SiO_2 exposed to carbon monoxide. The present band at 1760–1800 cm^{-1} might be more correctly assigned to CO(ads) which is multicentre-bonded to the exposed ruthenium surface (*4*). However, the maximum at 1750 cm^{-1} [Figs. 1, 2] for Ru/SiO_2 exposed to CO/H_2 mixtures resembles a maximum at 1750 cm^{-1} for CO on Ru/Al_2O_3 (*18*). The latter was ascribed to a μ-bonded carbonyl complex in which both the carbon and oxygen atoms in each adsorbed CO molecule were coordinated to the ruthenium surface. As here for Ru/SiO_2, the species responsible for the band at 1750 cm^{-1} for Ru/Al_2O_3 was reactive with hydrogen.

It is generally found for Ru/Al_2O_3 that the coadsorption of hydrogen and carbon monoxide leads to a lower band position for the linear RuCO than for adsorption of CO alone (*8*, *9*). However, the band position was identical here for the adsorption of CO alone or CO/H_2, suggesting that under the present conditions the presence of hydrogen was not having any effect on the strength of the C–O bond in surface RuCO. Furthermore, raising the temperature led to a band shift to 2026 cm^{-1} both for CO/H_2 and CO alone, again suggesting a passive role of hydrogen. Ekerdt and Bell (*12*) also noted that coadsorption of CO and H_2 on Ru/SiO_2 gave no shift in the CO band position. A clear difference between the results for Ru/SiO_2 in CO alone and in CO/H_2 was only apparent here by the appearance of an additional band at 2010 cm^{-1} for CO/H_2 and temperatures above 523 K. This shift is similar to that observed for Ru/Al_2O_3 in CO/H_2 (*8*, *9*). A tentative suggestion would be that the $\Delta\nu_{CO}$ effect for Ru/SiO_2 is not observed unless hydrogen is present under conditions for which some dissociative absorption of CO occurs. The resulting O-adatoms may have the same influence on vicinal Ru atoms as interactions between Ru and O^{2-} ions in the alumina surface for Ru/Al_2O_3 catalysts. The retention of a band at 2026 cm^{-1} while the band at 2010 cm^{-1} appeared showed that a high proportion of the Ru surface retained linearly adsorbed CO in an environment which was unaffected by adsorbed hydrogen. The adsorption of CO at high pressure would inhibit hydrogen adsorption.

Adsorbed Hydrocarbon Groups

Previous spectra of supported Ru exposed to CO/H_2 generally contained dominant bands ascribed to CH_2 groups and a weaker maximum due to CH_3 groups (*8–12, 18*). A band here at 2960–2970 cm^{-1} is assigned to CH_3-groups. Pairs of bands at 2917 and 2851 cm^{-1} [Fig. 1] and 2931 and 2857 cm^{-1} are assigned to two distinguishable types of CH_2 group. Both band pairings were present in Fig. 3(b). King (*9*) also reported two pairs of bands at 2922 and 2852 cm^{-1} and at 2930 and 2860 cm^{-1} in spectra of Ru/SiO_2 exposed to a flow of CO/H_2. The present bands at 2931 and 2857 cm^{-1} are ascribed to CH_2 segments of alkyl chains (*11*) which are unperturbed by the catalyst surface but which may be chemisorbed to Ru via a single CH_2 end segment (*9*). Termination of chain growth and desorption under static high-pressure conditions should lead to retention of longer chain hydrocarbons (e.g., CH_2/CH_3 = ca. 20/1 (*11*)) within the interstices of catalyst pellets or the pores of the silica support and additional contributions to the intensities of the bands due to CH_2 groups would result. The bands at 2917 and 2851 cm^{-1} which dominated the spectra when very little hydrocarbon had been formed [Fig. 3(a)] are ascribed to CH_2 segments involved in direct interaction with the metal surface.

An infrared band at 2981 cm^{-1} [Figs. 3, 5, 6] resembles a similar band in spectra of ethoxy groups on the surface of silica (*17*). The band was particularly strong for a 1 : 14 ratio of $CO : H_2$. It is unlikely (10) that ethanol was a prime product of reaction over Ru giving spillover to the silica surface (*17*) with the generation of ethoxy groups. An alternative would be that ethene formation (*6*) might be a precursor of ethoxy groups.

(*a*) *Effect of temperature*. The temperature sensitivity of the growth of bands due to adsorbed hydrocarbon was dependent on the total reaction pressure and the $CO : H_2$ ratio. For 30 bar (1 : 2 ratio) band growth was faster at 553 K than 503 K, but raising the temperature from 503 to 553 K for 15 bar (1 : 14, 1 : 2, or 14 : 1 ratios) decreased the rate of appearance of adsorbed hydrocarbon. In contrast, the rate of formation of methane was consistently higher at higher temperature. These results are compatible with previous observations (*9–11*). Enhanced selectivity to methane with increasing temperature is also consistent with the higher activation energy for methane formation than for total hydrocarbon formation (*23*). The anomalous result for the temperature effect at 30 bar suggests a dominating influence of pressure which favours higher hydrocarbon formation (*13*) even at high temperature. The band at 2981 cm^{-1}, attributed to ethoxy groups on silica, was most clearly recognised for $CO : H_2$ at 15 bar and a 1 : 14 ratio at 503 K [Fig. 6(c)] but was absent from the spectrum after reaction at 473 K [Fig. 6(d)]. Increased temperature should favour Fischer–Tropsch synthesis rather than alcohol synthesis (*13*), and therefore this supports the proposal that ethoxy groups were not formed as a result of ethanol synthesis in the present system. Ethene formation over Ru (*6*) may precede reaction with SiOH groups at high temperature to give unreactive (*24*) SiOEt groups. Spillover of alkenes from Ru catalyst to the alumina support in Ru/Al_2O_3 has been argued to precede spillover of H atoms which react with hydrocarbon to give saturated species observed by infrared spectroscopy (*18*).

(*b*) *Effect of pressure*. The effect of increasing pressure from 3 to 15 to 30 bar at a 1 : 2 ratio of $CO : H_2$ was to increase the rate of formation of adsorbed hydrocarbon species and to decrease the rate of formation of methane. Yamasaki *et al.* (*11*) showed that at low (<1 bar) CO and H_2 pressures the growth of infrared bands due to CH_2 groups depended positively (0.7–0.8 orders) on the partial pressures of H_2 and CO. However, reaction orders for product formation from CO/H_2 mixtures over ruthenium catalysts are dependent on both pressure and temperature (*4*, *23*). The formation of methane in particular often gives a negative reaction order in CO partial pressure, especially at high pressures (*1*, *12*, *23*). Separate reaction orders were not measured in the present work. However, the effects of varying total pressure at a constant CO : H_2 ratio suggest that the inhibiting effect of CO on hydrogen adsorption (*12*) apparently favoured selectivity towards the generation of higher hydrocarbons rather than methane and did not retard the increasing rate of CH_2 chain growth with increasing total reaction pressure despite retarding the rate of formation of methane.

(*c*) *Effect of CO/H_2 ratio.* Changing the CO : H_2 ratio from 1 : 14 to 1 : 2 to 14 : 1 at constant total pressure (15 bar) led to decreasing methane formation at both 503 and 553 K. This is consistent with the positive reaction order in hydrogen and the negative reaction order in CO reported for methane formation from CO/H_2 at moderate to high pressures (*4*, *12*, *23*). Increasing the CO : H_2 ratio should favour C–C chain growth leading to higher hydrocarbons (*12*, *13*). Changing from a 1 : 14 ratio to 1 : 2 was consistent with this expectation, the intensity of bands due to adsorbed hydrocarbon being more intense for the 1 : 2 ratio at both 503 and 553 K. Increasing the ratio further to 14 : 1 at either temperature gave a decrease in the extent of higher hydrocarbon formation, possibly because hydrogen was unable to compete for surface sites in the presence of a vast excess of CO. Despite this, selectivity to higher hydrocarbon at the 14 : 1 ratio was increased because the extent of methane production had become undetectable. The ratio of the band intensities at 2931 and 2857 cm^{-1} to the intensity at ca. 2960 cm^{-1} was also greater for the 14 : 1 mixture [Fig. 8] than for the 1 : 14 or 1 : 2 mixtures [Figs. 4 and 7] showing that a longer-chain product had been generated and supporting the contention (*13*) that C–C chain growth should be favoured in a CO-rich feedstock.

Factors Affecting Catalyst Activity and Reaction Mechanism

The position of the infrared band for linearly adsorbed CO on ruthenium *in situ* during reaction with CO/H_2 mixtures was apparently independent of the composition and total pressure of the reactant mixture. A similar result has been reported for a less varied range of mixture compositions and low pressures (<1 atm) (*12*). However, the suggestion (*12*) that there was no band shift during reaction is not consistent with either the present results or previous observations (*8*, *9*, *11*). The band shift and weakening of the RuCO band with time is generally attributed to the electronic effects of surface carbon on vicinally adsorbed CO molecules and to partial blocking of CO adsorption sites (*8*, *11*). King (*9*) argued that the shift might have arisen because the carbon deposit blocked the weakest Ru sites for CO adsorption and therefore the high-wavenumber side (weak Ru–C bond, therefore stronger C–O bond) of the ν_{CO} band was removed, giving an apparent shift in band maximum to lower wavenumbers. This is not a tenable conclusion here because it would require that the apparent shift occurred within the confines of the overall band envelope before reaction commenced. The results [Fig. 1] show enhanced absorption intensity on the low wavenumber side of the band envelope, suggesting that a high proportion of the linearly adsorbed CO molecules had been perturbed by deposited reaction products or intermediates and therefore the infrared band as a whole had shifted to lower wavenumber. Sintering of ruthenium during reaction (*6*) could also have contributed to the progressive weakening of the intensities of infrared bands due to adsorbed CO.

The complete reaction of linearly adsorbed CO on Ru/SiO_2 with hydrogen in the absence of carbon monoxide is consistent with the proposal that linearly adsorbed CO is a reaction intermediate in hydrocarbon synthesis over ruthenium catalysts (*6*). The present results also support the analogous result for Ru/Al_2O_3 that μ-bonded carbonyl groups (band at 1750 cm^{-1}) are reactive towards hydrogen (*18*). Although methanol is not a product of the present reactions it is relevant to note that μ-bonded CO on Ru has been proposed as an essential intermediate in the hydrogenation of CO to methanol (*25*) and was here observed from methanol decomposition on Ru/SiO_2. Methanol decomposes on Ru(001) to give CO(ads) and H(ads) (*25*). The present infrared spectra of methanol and ethanol adsorbed on Ru confirm that dissociative adsorption gives linearly adsorbed CO. Again, as for the adsorption of CO/H_2 mixtures or CO alone, alcohol adsorption on Ru/SiO_2 also gave a bridging CO species, possibly in the μ-bonded configuration (*18*). The band at 2981 cm^{-1} in spectra of adsorbed ethanol is due to a vibration of ethoxy groups on silica (*17*) and leads to the same assignment for a similar band in spectra of Ru/SiO_2 exposed to CO/H_2 mixtures. The additional bands at 1457 and 1397 cm^{-1} in spectra of adsorbed ethanol would have contributed to the maxima at 1460 and 1395 cm^{-1} in spectra after CO/H_2 reaction, although the 1460 cm^{-1} band in particular would have been partly attributable to vibrations of CH_2 groups in alkane chains. Possible bands at 2938 and 2906 cm^{-1} due to ethoxy groups following CO/H_2 reactions were obscured by maxima due to other adsorbed products of reaction.

Mechanisms for CO/H_2 reactions involving direct hydrogenation of nondissociatively adsorbed CO in the first step have been proposed (*1, 26*). However, there is compelling evidence for mechanisms of Fischer–Tropsch synthesis which involve dissociative adsorption of CO followed by hydrogenation of surface carbon to give adsorbed CH species which are further hydrogenated to hydrocarbon products (*12, 27*). The present results not only support the proposal that molecularly chemisorbed CO is a precursor of active intermediates in the reactions but also agree with suggestions that surface hydrocarbonaceous and carbon species are further hydrogenated to give methane (*1, 9, 11, 12*). Figure 1 exemplifies the result that loss of CO(g) in reacting systems led to subsequent loss of linear RuCO and μ-bonded CO on Ru and the attenuation of infrared bands due to the CH groups. However, reports vary as to whether (*11*) or not (*10, 12*) the hydrocarbon constitutes an intermediate in the formation of desorbed reaction products. King (*10*) reported two types of CH_2 group, one of which was reactive towards hydrogen, the other being unreactive. The reactive type of CH_2 gave bands at 2922 and 2852 cm^{-1}. The equivalent species giving maxima at 2917 and 2851 cm^{-1} here was not completely removed after reaction in excess hydrogen at 553 K for 19 h [Fig. 1(i)–(k)]. The reactivity of this species was apparently significant while CO(g) or CO(ads) remained in the system but fell to zero in the absence of CO. However, the residual level of band intensities [Fig. 3(a)] would be expected [Fig. 3(c)] in view of the amount of methane present in the system after the depletion of CO [Fig. i(j)]. The results here therefore support the conclusion (*10*) that methylene species bonded to ruthenium are hydrogenated giving methane as product.

The generation of traces of carbon dioxide at 553 K under two of the sets of present experimental conditions probably arose from reaction between CO(g) and oxygen atoms generated by dissociative adsorption of CO (*28*). Carbon dioxide itself would be expected to be hydrogenated giving methane and higher hydrocarbons (*29*). The removal of oxygen atoms from the ruthenium surface also led to water which was largely desorbed from the surface under reaction conditions. A weak band due to water generally appeared in spectra at ca. 1630 cm^{-1}.

CONCLUSIONS

(a) In contrast to ruthenium supported on alumina (*19, 21, 22*), ruthenium supported on silica in CO/H_2 mixtures at 295–723 K remained in the zero oxidation state not only at high temperatures (as for alumina) but also at low temperatures for which ruthenium on alumina undergoes disruptive oxidation.

(b) A shift in the linear ν_{CO} RuCO band with time towards lower wavenumbers cannot be attributed to selective site blockage of the weakest Ru sites for CO adsorption (*9*) but is probably due to the perturbation of linearly adsorbed CO molecules by coadsorbed reaction products or intermediates derived from CO, H_2 or both CO and H_2.

(c) Ru sites in Ru/SiO_2 exposed to CO/H_2 mixtures at high temperature are partially blocked by the build-up of adsorbed intermediates or products on the ruthenium surface.

(d) Both linearly adsorbed CO on ruthenium and a μ-bonded carbonyl complex of Ru (*18*) in Ru/SiO_2 were reactive with hydrogen at high temperature and pressure.

(e) Dominant products from CO/H_2 over Ru/SiO_2 were methane and higher hydrocarbons, the rate of formation of methane being increased by raising the temperature, lowering the total reaction pressure or increasing the proportion of H_2 in the CO/H_2 mixture. Increasing pressure or $CO:H_2$ ratio favoured C–C chain growth and the formation of higher hydrocarbons.

(f) Hydrocarbonaceous products on Ru may act as intermediates undergoing further reaction with hydrogen giving methane.

ACKNOWLEDGMENTS

We thank SERC for a Studentship and a grant for the spectrometer, BP Chemicals (Hull) for collaboration through the CASE scheme, and Dr. R. D. Oades for helpful discussions.

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