

Comparative FT–IR and MAS NMR Spectroscopic Studies of Rh/SiO₂ Catalysts Exposed to CO/H₂ at High Temperature and Pressure

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¹³C and ¹H MAS NMR spectra of Rh/SiO₂ catalysts after exposure to methanol and ethanol at 473 K or to CO:H₂ mixtures at 15 atm (ratios 1:14, 1:2, and 14:1) and 473, 523, or 553 K are reported. The NMR spectra complement FT–IR spectra and confirm that adsorbed OMe and OEt groups resulting from CO/H₂ reactions over Rh/SiO₂ exist predominantly on the silica surface. NMR was better than FT–IR for distinguishing adsorbed OMe, OEt, and hydrocarbon species and also enabled identification of immobile chemisorbed species and weakly adsorbed mobile product molecules. Changes in the CO:H₂ ratio had a profound effect on the nature of resulting surface species *in situ* under reaction conditions. © 1992 Academic Press, Inc.

INTRODUCTION

In situ FT–IR spectroscopic study of CO/H₂ reactions over Rh/SiO₂ catalysts has led to the recognition of infrared bands which may be ascribed to adsorbed methoxy, ethoxy, acyl, and alkyl groups on the catalyst surface during reaction (1–4). However, bands due to CH-stretching vibrations of these groups fall in a narrow spectral range and therefore there is considerable overlap, or even coincidence, of the bands for different species. For example, the band maxima occurred at 2981–2978, 2944–2940, and 2904–2900 cm⁻¹ for ethoxy groups, 2956 and 2857 cm⁻¹ for methoxy groups, and 2933 and 2857 cm⁻¹ for methylene groups on 4.6% Rh/SiO₂ exposed to CO (5 atm)/H₂(10 atm) at 503–553 K (3). Clear identification of adsorbed product species is therefore difficult, particularly when bands due to one product are obscured by overlapping maxima due to another. Furthermore, it is desirable to be able to recognise whether the adsorbed species *in situ* during reaction exist on the surface of the rhodium or the oxide support. The appearance of methoxy and ethoxy groups for Rh/SiO₂ involves catalysis on the metal but the resulting groups exist on the silica support (2–4). Similar spe-

cies which may have existed on rhodium could not be detected possibly because resulting infrared bands were totally obscured by much more intense maxima due to the alkoxy groups chemisorbed on the silica. The present study was aimed at testing whether MAS NMR spectra of Rh/SiO₂ after treatment with CO/H₂ at high temperature and high pressure may enable gain of complementary or additional information about the surface species present during reaction.

EXPERIMENTAL

Catalyst containing 2.3 wt% Rh on silica was prepared by reduction (3.5 v/v% H₂ in Ar, 0.1 MN m⁻², 200 cm³ min⁻¹, 773 K, 1 h) of self-supporting discs of Rh(NO₃)₃/SiO₂ mounted in a stainless-steel infrared cell fitted with fluorite windows and pressure tested (by ICI Catalyst Research Centre) to 175 atm. The supported salt was prepared by drying an aqueous dispersion (383 K, 16 h) of silica (Grace grade 432) and rhodium(III) nitrate (Johnson Matthey) and was then compressed (7 ton on die) into discs of 100 mg mass and 25 mm diameter. After reduction and evacuation (773 K, 30 min) of mounted discs and cooling to reaction temperature (473, 523, or 553 K) the catalyst was exposed to a CO/H₂ mixture at total

pressure 1.5 MN m⁻² (15 atm) and the FT-IR spectrum was recorded as a function of time using a Perkin-Elmer 1750 Fourier transform infrared spectrometer linked to a 7300 computer. Spectra were also recorded of silica alone and Rh/SiO₂ exposed at 473 K to a flow of argon saturated with methanol or ethanol vapour. More complete details of catalyst preparation and characterisation are given elsewhere (4). Good quality infrared spectra were best obtained with a 100-mg disc (diameter 2.5 cm) in the cell. However, this did not provide enough catalyst for the NMR spectroscopy, which therefore involved examination of Rh/SiO₂ (400 mg) from four discs that had been simultaneously exposed to reactant gases under *in situ* high *T* and *P* conditions in the infrared cell. After significant buildup of surface species had occurred, as monitored by recording infrared spectra, the 400-mg sample was transferred (via brief exposure to the ambient laboratory atmosphere) to a 7-mm-outside-diameter zirconia NMR rotor. The transfer of the sample via air is open to criticism as some surface species may have undergone reaction during transfer. However, the present MAS NMR spectra wholly support the conclusions derived from FT-IR results for the catalyst samples *in situ* under reaction conditions. The relevant surface species containing hydrocarbon groups were unaffected by brief (ca. 10 s) exposure to air.

NMR spectra were recorded on a Bruker AM300/WB FT NMR spectrometer fitted with a Bruker HP WB 73A MAS accessory. Samples were spun at speeds between 3 and 4 kHz. ¹³C spectra were measured at 75.5 MHz. Where cross-polarisation (CP) was used the pulse angle ($\pi/2$) was 5.3 μ s and contact time was 500 μ s. Spectra recorded without CP used a 2- μ s pulse angle. All ¹³C spectra were accumulated using an acquisition time of 0.01 s (TD = 400 w) and a receiver delay of 1 s (sweep width = 270 ppm). The number of scans was sample dependent varying from 1000 to 56000. Spectra were zero filled to 16 K and transformed after 5

Hz line broadening. Shifts are reported with respect to external tetramethylsilane (TMS).

¹H spectra were measured at 300.1 MHz; pulse angle 30° = 3 μ s; accumulation time = 0.14 s; number of scans = 32; sweep width = 100 ppm. These were accumulated in and transformed from 8 K memory, no line broadening. Shifts were measured relative to external TMS.

RESULTS

The expectation that methanol and ethanol, as products of CO/H₂ reactions over Rh/SiO₂, were precursors of chemisorbed methoxy and ethoxy groups on silica prompted initial NMR experiments for methanol and ethanol adsorbed on SiO₂ alone and Rh/SiO₂ at 473 K. Silica alone was subjected to a reduction procedure identical to that adopted for Rh/SiO₂ before exposure to alcohol vapours. The dominant bands at 2958 and 2857 cm⁻¹ in the infrared spectrum of MeOH on silica at 473 K (Fig. 1a) have been previously ascribed to vibrations of methoxy groups covalently bonded to the silica surface (3, 5). Subsequent cooling to room temperature gave under cross-polarisation conditions a ¹³C NMR spectrum with a single resonance at 47.9 ppm due to the same methoxy groups (Fig. 1b). However, with no cross-polarisation there was also a single absorption at 47.0 ppm (Fig. 1c), which may be attributed to a mobile adsorbed methanol species. Cooling the catalyst discs in the static atmosphere in the infrared cell, before transfer to the NMR spectrometer, had apparently led to physical adsorption possibly involving multilayers on the oxide surface. This was confirmed by the ¹H NMR spectrum (Fig. 1d), which contained a dominant resonance at 3.3 ppm attributed to CH₃ groups in mobile methanol molecules with a tail towards higher ppm due to unreacted SiOH groups on the silica surface.

Results for MeOH on Rh/SiO₂ were similar to those for MeOH on SiO₂ with respect to both the infrared spectrum (4) and the

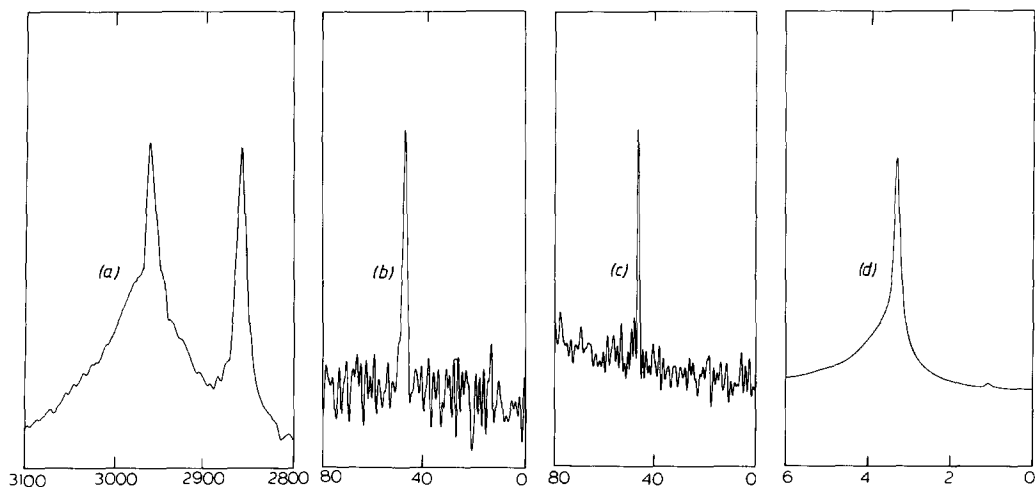


FIG. 1. (a) Infrared (wavenumber (cm^{-1}) vs intensity), (b) ^{13}C NMR (with cross-polarisation) (ppm vs intensity), (c) ^{13}C NMR (no cross-polarisation) (ppm vs intensity), and (d) ^1H NMR spectra of silica exposed to methanol (473 K) (ppm vs intensity). The infrared and NMR spectra were recorded with the sample at high temperature and room temperature, respectively.

existence of a single ^{13}C NMR resonance at 47.7 ppm due to immobile chemisorbed OMe groups. The ^{13}C NMR signal with no cross-polarisation and the ^1H NMR spectrum again provided corroborative evidence for the presence of adsorbed mobile methanol molecules. The small difference between the peak positions for methanol adsorbed on silica and Rh/SiO₂ is not deemed to be significant in view of the difficulties of accurately referencing MAS spectra.

Adsorption of ethanol on silica (Fig. 2a) and Rh/SiO₂ (Fig. 3a) gave nearly identical infrared spectra with bands at 2981, 2938, and 2906 cm^{-1} due to vibrations of chemisorbed ethoxy groups on silica at 473 K. The ^{13}C NMR spectra contained peaks at 58.5 and 14.2 ppm for silica and at 58.1 and 14.0 ppm for Rh/SiO₂ due to CH₂ and CH₃ groups in the same chemisorbed ethoxy groups (Figs. 2b and 3b). Again the presence of mobile adsorbed alcohol molecules was shown by pairs of maxima at 56.9 (CH₂) and 14.5 (CH₃) for ethanol on silica (Fig. 2c) and at 56.6 (CH₂) and 14.4 (CH₃) ppm for ethanol on Rh/SiO₂ (Fig. 3c) in the absence of cross-polarisation. The ^1H NMR spectra similarly exhibited two strong lines at 3.6 ppm (CH₂)

and 1.0 ppm for silica (Fig. 2d) and at 3.6 and 1.1 ppm for Rh/SiO₂ (Fig. 3d). These may also be ascribed to mobile adsorbed ethanol molecules. However, there were some weak additional peaks in the ^1H NMR spectra of adsorbed ethanol on Rh/SiO₂. These peaks, which were absent from spectra of ethanol on silica alone, were at 1.9, 2.0, 3.9, 4.8, 5.8 (Fig. 3d), and 9.3 ppm.

Figure 4 shows results for Rh/SiO₂ which had been heated at 473 K in a 1 : 14 ratio of CO : H₂ at a total pressure of 15 atm. The infrared spectrum has a high noise level because it was recorded with $4 \times 100\text{-mg}$ discs in the infrared cell during preparation of the catalyst for NMR spectroscopy. The considerably better signal-to-noise ratio for 100-mg discs is exemplified by the spectrum in Fig. 3. Detailed infrared data for 100-mg catalyst discs will be presented elsewhere (4). The present FT-IR spectra for a 400-mg sample, in accordance with results for 100-mg discs (4), contain main maxima at 2988, 2958, ca. 2940(sh), and 2857 cm^{-1} (Fig. 4a) which suggest the presence of both methoxy and ethoxy groups on the catalyst surface. The ^{13}C NMR spectrum (Fig. 4b) provides conclusive evidence for this suggestion with

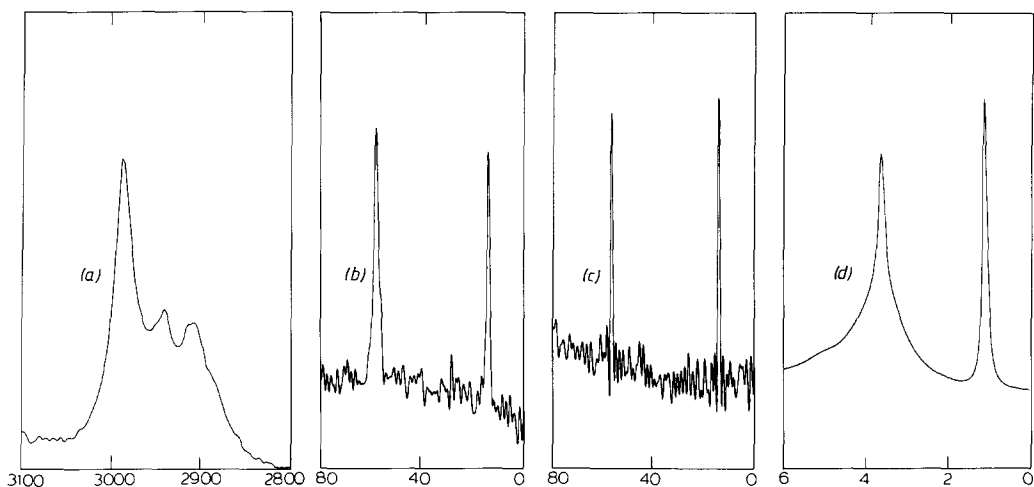


FIG. 2. (a-d) As in Fig. 1 but for silica exposed to ethanol (473 K).

peaks at 47.7 ppm due to immobile methoxy groups and at 58.1 (CH₂) and 14.3 (CH₃) ppm due to immobile ethoxy groups. The relative intensities of these peaks suggest that roughly equal populations of the two species were chemisorbed on the silica support. Furthermore, an additional weaker line above the noise level at 29.8 ppm may be assigned to CH₂ groups in methylene chains of adsorbed hydrocarbon species. The corresponding expected infrared bands at 2933

and 2857 cm⁻¹ for these species (3) were obscured in the infrared spectra by the bands due to OMe and OEt groups on silica. The ¹³C NMR spectrum without cross-polarisation was featureless (Fig. 4c) pointing to the absence of mobile alcohol molecules on the Rh/SiO₂ surface. The ¹H NMR spectrum (Fig. 4d) was dominated by the broad maximum due to SiOH groups but also exhibited very weak bands possibly due to some mobile alcohol.

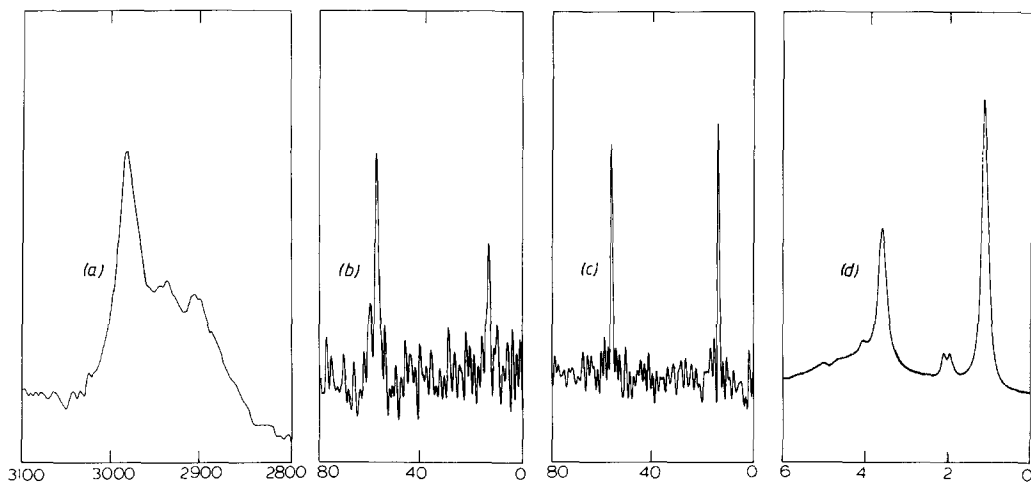


FIG. 3. (a-d) As in Fig. 1 but for Rh/SiO₂ exposed to ethanol.

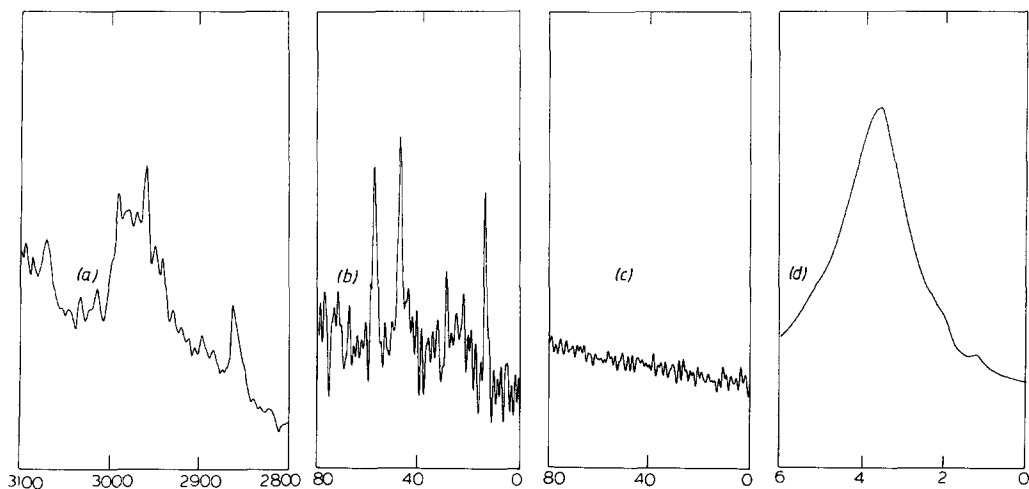


FIG. 4. (a-d) As in Fig. 1 but for Rh/SiO₂ exposed to CO (0.1 MN m⁻²)/H₂ (1.4 MN m⁻²) at 473 K for 70 h.

The infrared spectrum of Rh/SiO₂ after exposure to a 1 : 2 ratio of CO : H₂ at a total pressure of 15 atm and 523 K well illustrates the problem of distinguishing individual surface species from overlapping infrared bands due to several adsorbed products of reaction (Fig. 5a). A band at 3016 cm⁻¹ was due to methane gas. The other main band maxima due to alkyl species were at 2981, 2961, 2938, ca. 2906, and 2857 cm⁻¹, again

suggesting that the main adsorbed products were methoxy and ethoxy groups. However, unlike the previous spectrum (Fig. 4a), the maximum at 2981 cm⁻¹ had become the most intense band suggesting that a higher proportion of OEt groups had been formed. The ¹³C NMR spectrum (Fig. 5b) not only more clearly distinguishes OEt (58.0 and 14.0 ppm) and OMe (47.5 ppm) groups but also supports the suggestion that the ethoxy

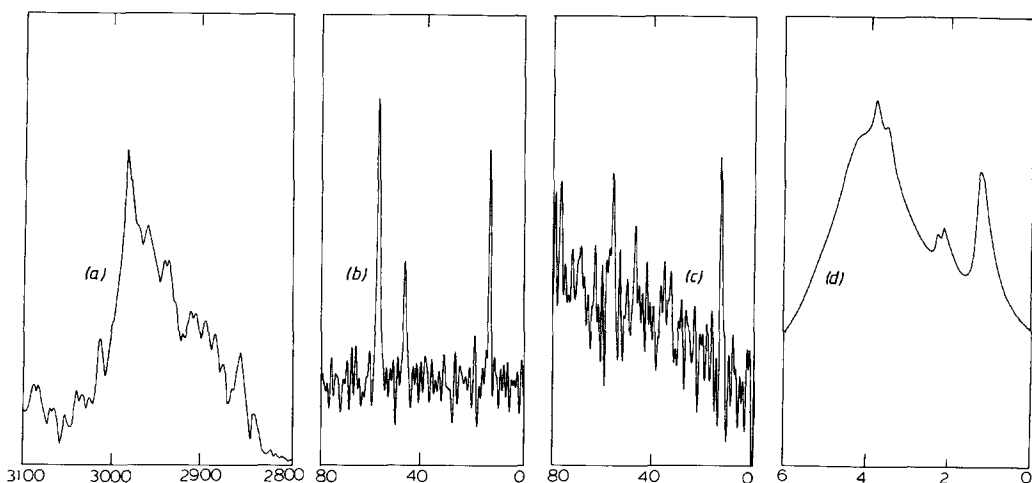


FIG. 5. (a-d) As in Fig. 1 but for Rh/SiO₂ exposed to CO (0.5 MN m⁻²)/H₂ (1.0 MN m⁻²) at 523 K for 70 h.

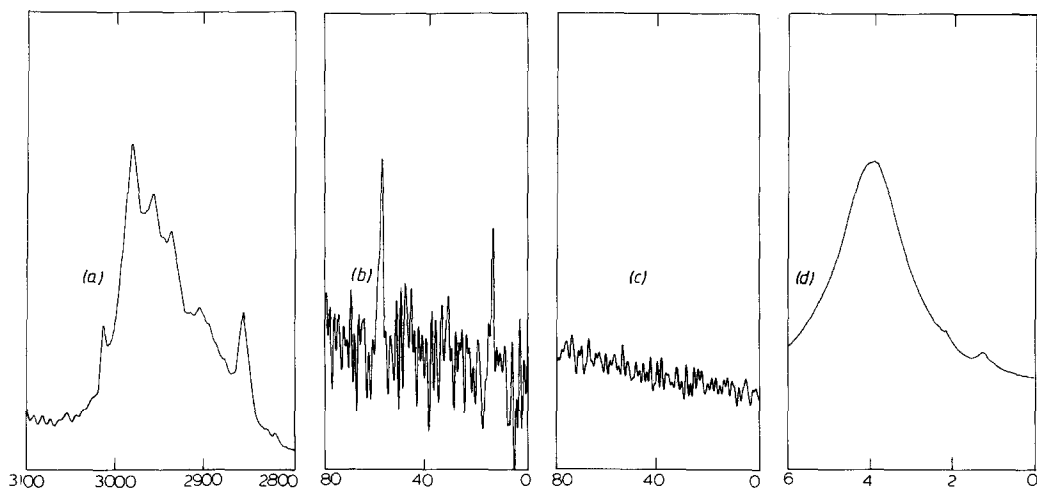


FIG. 6. (a-d) As in Fig. 1 but for Rh/SiO₂ exposed to CO(0.5 MN m⁻²)/H₂ (1.0 MN m⁻²) at 553 K for 20 h.

species were dominant. Without cross-polarisation the peak at 13.6 ppm (Fig. 5c) together with a line scarcely discernible above the noise at ca. 56.7 ppm suggests the presence of weakly adsorbed mobile ethanol molecules as a reaction product (Fig. 5c). A slight hint of a weak line at ca. 47.0 ppm may indicate that some methanol is also present. The ¹H NMR spectrum (Fig. 5d) contained peaks at 1.0 and 3.6 ppm due to mobile ethanol molecules (Fig. 3d) and a shoulder at 3.3 ppm due to weakly adsorbed mobile methanol (Fig. 1d). Also recorded were lines at 1.9, 2.1, and 9.3 ppm, which were present in the spectrum of Rh/SiO₂ after exposure to ethanol vapour at 473 K (Fig. 3d).

Results for a second sample of Rh/SiO₂ exposed to CO (0.5 MN m⁻²)/H₂ (1.0 MN m⁻²) but at 553 K are shown in Fig. 6. The infrared spectrum suggested that less methoxy relative to ethoxy species was formed than in the corresponding reaction at 523 K (Fig. 5). This was borne out by the ¹³C NMR spectrum (Fig. 6b) in which the dominant resonances at 58.2 and 14.5 ppm were due to immobile ethoxy groups. The ¹³C NMR (without cross-polarisation) and ¹H NMR spectra (Figs. 6c and 6d) showed that very little mobile ethanol had

been retained on the surface after treatment at 553 K.

The infrared spectrum of Rh/SiO₂, which had been exposed to a CO:H₂ mixture of 14:1 at a total of 15 atm pressure, showed little evidence for OMe and OEt groups but contained two maxima at 2933 and 2857 cm⁻¹ (Fig. 7a), which may be ascribed to CH₂ groups in alkyl chains (3, 6). The ¹³C NMR spectrum (Fig. 7b) with cross-polarisation fully supported this result with a single sharp maximum at 28.8 ppm attributable to CH₂ groups in alkyl chains. Although not shown in Fig. 4, the appearance of a line due to alkyl CH₂ groups was accompanied for a 1:14 ratio of CO:H₂ by a broad maximum at ca. 130 ppm which was absent for spectra not containing the absorption due to CH₂ groups (Figs. 1-3, 5, 6). The broad resonance centred at 127.4 ppm was much more intense for a CO:H₂ ratio of 14:1 (Fig. 7b) and may be tentatively ascribed to an aromatic-like unsaturated hydrocarbonaceous material formed on the catalyst surface. The ¹³C NMR spectrum with no cross-polarisation and the ¹H NMR spectrum (Fig. 7d) showed that mobile surface species were undetectable. The ¹H NMR signal was a single band due to SiOH groups on the oxide support.

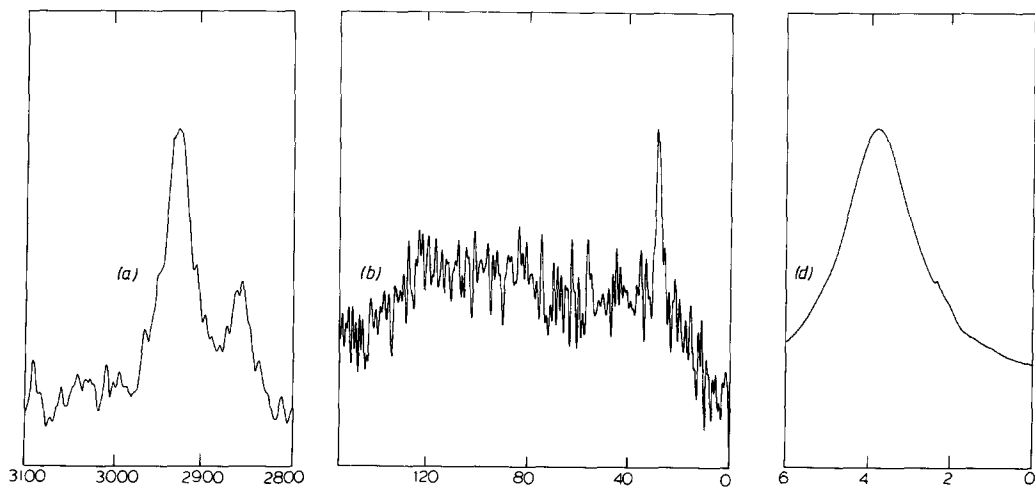


FIG. 7. (a, b, and d). As in Fig. 1 but for Rh/SiO₂ exposed to CO (1.4 MN m⁻²)/H₂ (0.1 MN m⁻²) at 553 K for 90 h.

DISCUSSION

The ¹³C NMR spectra confirm previous (3, 4) interpretations of infrared bands due to adsorbed saturated alkyl species on Rh/SiO₂ after reaction with CO/H₂ mixtures at high temperature and pressure. The NMR data give better separation of signals due to different species than the overlapping infrared bands. The NMR results are also consistent with the conclusion (2-4) that the adsorbed methoxy and ethoxy groups generated by reaction of CO and H₂ over rhodium predominantly exist on the surface of the silica support. The methoxy and ethoxy groups on silica were not desorbed by subsequent evacuation at reaction temperature and therefore it is unlikely that they constitute intermediates in the catalytic conversion of CO/H₂ mixtures to methanol and ethanol, which are formed by catalysis over rhodium and subsequently are chemisorbed on the silica support until the oxide surface becomes saturated with alkoxy groups. However, the alkoxy groups may be reacted or displaced by contact with CO at high temperature (3).

An added advantage of NMR is its ability to distinguish mobile and immobile species containing common functional groups. In

the solid-state NMR experiment, resonances from mobile species cannot be seen when cross-polarisation is applied; conversely they are accentuated when CP is not used, thus allowing differentiation to be made. If the mobile and immobile species have nearly coincident infrared bands then the distinction between the species using infrared spectroscopy may only be achieved by careful study of spectra as a function of surface coverage during adsorption or desorption. However, the infrared method does have the advantage of allowing *in situ* study of catalysts under high temperature and pressure reaction conditions, whereas MAS NMR requires transfer of catalyst to the rotor in the NMR spectrometer. In the present study the species observed by NMR for Rh/SiO₂ at ambient temperature and pressure were also observed using FT-IR spectroscopy for the Rh/SiO₂ at 15 atm and 473-553 K showing that the species were not destroyed on transfer even when involving brief exposure to air. Confirmation of this conclusion was achieved in two ways. First, four discs mounted in the infrared cell and treated with CO/H₂ under reaction conditions gave infrared spectra with a poor signal-to-noise ratio because of the high ab-

sorbing and scattering characteristics of Rh/SiO₂. Three discs were then removed from the cell and the spectrum of the remaining disc, which had been briefly exposed to air, was recorded. Bands in the ν_{CH} and δ_{CH} spectral regions were identical in position and relative intensities for the four discs and the single disc, although the signal-to-noise ratio for the latter was much better. Second, corresponding spectroscopic identity was observed for catalyst which was removed from the infrared cell and powdered for MAS NMR examination, after which it was re-pressed into a disc (in air) and its infrared spectrum was rerecorded. Detectable CH species on the catalyst surface were unaffected by brief contact with air. Details of the FT-IR results in other spectral regions are given elsewhere (4) and allow conclusions to be drawn concerning surface silanol groups on the silica support and adsorbed forms of CO on rhodium during the *in situ* CO/H₂ reactions. Observation of the latter by NMR would have required transfer of catalyst to the rotor under controlled air-free conditions.

Selectivity to particular oxygenate or hydrocarbon products formed from CO/H₂ reactions over rhodium catalysts may depend on temperature (7-9) and the CO/H₂ ratio (8). A temperature effect is shown here by the results for CO(5 atm)/H₂(10 atm) at 523 and 553 K. The selectivity to ethanol rather than methanol was greater at 553 K than at 523 K. This contrasts with results for a total pressure of 3 atm for which product selectivity, as detected by FT-IR spectra of adsorbed OEt and OMe groups, was insensitive to temperature (4). The difference in temperature sensitivity of EtOH/MeOH selectivity for 1:2 ratios of CO:H₂ at total pressures of 3 and 15 atm can only be qualitatively inferred from the FT-IR data, particularly because bands due to CH₂ groups in alkyl chains also contributed to the spectra for Rh/SiO₂ in CO/H₂ at 3 atm (4). However, the conclusions are corroborated by the ¹³C NMR data for CO/H₂ reaction at 15 atm, which show that the relative intensity

of the methoxy and ethoxy resonances changed markedly (Fig. 5b and 6b) in the sense that selectivity to ethoxy species was enhanced, relative to methoxy species, on increasing the temperature of Rh/SiO₂ in CO/H₂ from 523 to 553 K.

The marked difference between the adsorbed product selectivities for CO:H₂ ratios of 1:14 and 14:1 may in part be due to the temperature change from 473 to 553 K. However, the dominant effect was due to the change in gas-phase composition (10). The H₂-rich mixture favoured MeOH and EtOH formation in approximately equal proportions with a trace of CH₂ groups in alkyl chains. The CO-rich mixture gave no MeOH or EtOH but only the species containing alkyl CH₂ groups. In accordance with the present result, heat treatment of the adsorbed products of CO/H₂ reaction over Rh/SiO₂ with CO alone promoted the appearance of infrared bands at 2933 and 2857 cm⁻¹ due to CH₂ groups (3). A similar but lesser effect also accompanied subsequent heat treatment in hydrogen alone at 523 (3).

It has been proposed that reactions of CO and H₂ over transition metal catalysts generate a hydrocarbonaceous or carbonaceous residue which is a precursor of at least some of the reaction products (11-17). The broad maximum centred at ca. 127 ppm for Rh/SiO₂ heated in a 14:1 mixture of CO:H₂ suggests that the presence of a heterogeneous mixture of unsaturated hydrocarbon species had been generated during the reaction. This mixture might be regarded as a hydrocarbonaceous residue. A subsequent reaction with hydrogen to generate saturated alkyl chains (i.e., 2933, 2857 cm⁻¹, NMR 28.8 ppm) is not ruled out by the present results. The data for a 1:14 mixture of CO:H₂ are also consistent with this possibility since a much weaker broadband at ca. 130 ppm was accompanied by infrared and NMR evidence for a low surface concentration of CH₂ groups in alkyl chains.

The additional weak bands in ¹H NMR spectra of Rh/SiO₂ after treatment with etha-

nol at 473 K (Fig. 3d) cannot be unambiguously ascribed to particular surface species. Signals at 5.8, 4.8, and 3.9 ppm could be attributable to alkenyl (4.8, 3.9 ppm) or tertiary CH (5.8, 4.8 ppm) species suggesting that decomposition of ethanol molecules had occurred. Infrared spectra have shown that ethanol further decomposes on Rh/SiO₂ to give adsorbed CO (3, 4). Oxidation of ethanol could be indicated by the peak at 9.2 ppm which is tentatively ascribed to a CHO group. The existence of the same peak for Rh/SiO₂ after treatment with CO(5 atm)/H₂(10 atm) at 523 K would be consistent with reports of adsorbed carbonyl species on Rh/SiO₂ after exposure to CO/H₂ at high temperature and pressure (1, 2, 9). The twin signals at 1.9 and 2.0 ppm were present in spectra of Rh/SiO₂ after exposure to ethanol (Fig. 3d) or a CO/H₂ mixture (Fig. 5d). Despite occurring in the region of the spectrum for CH₂ groups in alkane chains this is an unlikely attribution of the signals because there was no evidence for alkane chains in either the ¹³C NMR or the infrared spectra. There is also doubt as to whether the peaks are due to two distinct types of ¹H atom or arise from the splitting of a single peak via coupling with an adjacent nucleus. Further experiments are required to test these alternatives and in particular to identify whether coupling of surface H atoms with rhodium nuclei might be responsible for generating a doublet in the spectrum.

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