The effect of carbon monoxide on the oligomerization of acetylene in hydrogen over a Ni/SiO$_2$ catalyst

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ABSTRACT

The effect of small amounts of carbon monoxide on the oligomerization of acetylene over a low loaded Ni/SiO$_2$ catalyst has been investigated. Although CO does not participate in the reaction it has two beneficial effects if oligomer products are desired. Conversion of acetylene is higher, both initially and over time, and the selectivity to C$_4$–C$_{10}$ product is improved relative to C$_2$ hydrogenation. Higher products are predominantly aliphatic alkenes. CO increases formation of branched products relative to linear ones and dienes relative to alkenes while suppressing benzene and higher aromatics. In the absence of CO, unsaturated products can be largely hydrogenated to alkanes if a Pt/SiO$_2$ catalyst is located immediately downstream the Ni/SiO$_2$ but the hydrogenation of dienes and trienes proceeds only as far as alkenes when the feed contains CO. The twin effects of CO can be interpreted on the basis that CO competes for nickel sites that would otherwise be able to accept hydrogen atoms from H$_2$ or C$_2$H$_2$. The Ni/SiO$_2$ catalyst was sensitive to feed impurities such as phosphine present in some grades of acetylene but deactivation was not complete.

1. Introduction

The conversion of natural gas to synthetic liquid fuels is a well-established process with commercial plants now operating in South Africa, Malaysia and Qatar and another very large plant under construction in Qatar. All use the Fischer–Tropsch route with methane converted first to a mixture of carbon monoxide and hydrogen (syngas) and then to hydrocarbons over an iron- or cobalt-based catalyst [1]. However the process is not well suited to small or medium sized offshore gas deposits because the size and nature of the plant precludes installation on floating platforms. A route that might be more suitable is the pyrolysis of methane to acetylene/ethylene mixtures followed by conversion to liquid fuel as patented recently by Hall et al. [2–4]. The initial report emphasised direct oligomerization of acetylene [5] but a later publication envisaged the selective hydrogenation of acetylene to ethylene followed by ethylene oligomerization [6].

The oligomerization of acetylene in a hydrogen carrier over high nickel content catalysts was first described in the 1930s and 1940s [7–10]. In recent work we have shown that 2% Ni/SiO$_2$ is more stable than catalysts containing more nickel on carriers such as

zeolites and alumina [11]. Complete conversion of acetylene was possible at temperatures as low as 140 °C with ca. 27% of the acetylene converted to C$_5$+ material, 15% to a C$_4$ fraction and most of the remainder to ethylene. This raised the possibility of using oligomerization to strip acetylene from a methane pyrolysis stream with the ethylene produced then further oligomerized to synthetic fuel in a second stage.

In addition to acetylene and ethylene, methane pyrolysis streams can contain carbon monoxide if water is used to moderate carbon formation and/or to quench the product stream at high temperature. The aim of the present work was to determine if these other components affected acetylene oligomerization over a low-loaded Ni/SiO$_2$ catalyst. Our previous work showed that the product distribution from the oligomerisation of acetylene in hydrogen alone was extremely complex with considerable quantities of branched and linear products and also of molecules with an odd number of carbon atoms [12]. Alkenes dominated, followed by alkanes and dienes with a low yield of aromatics. The present studies show that carbon monoxide affects this distribution in a beneficial way—both in terms of product distribution and in terms of catalyst activity over time.

2. Experimental

Full details of the catalyst preparation, characterisation, testing and analytical procedures can be found in reference [12]. In essence,

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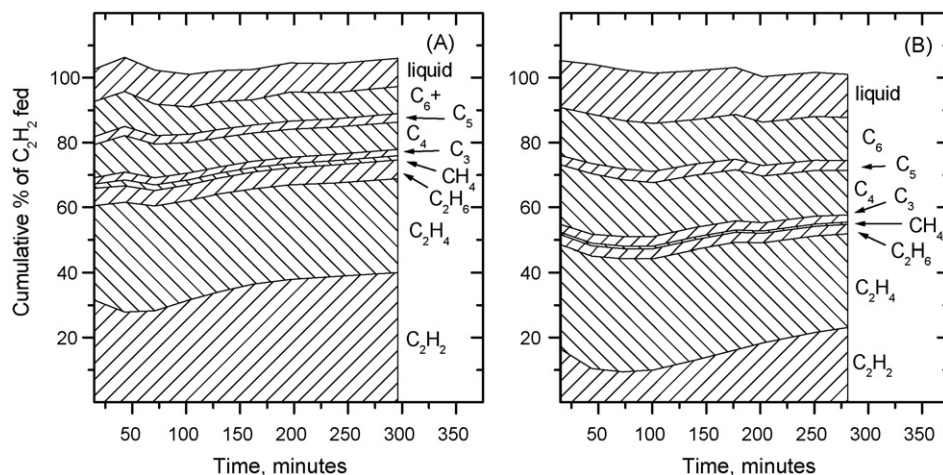
Fig. 1. Product distribution versus time on stream for reaction over Ni/SiO$_2$ at 200 °C in the absence and presence of carbon monoxide. (A) With feed comprising 25% C$_2$H$_2$/65% H$_2$/10% N$_2$ with total flow rate of 50 cm^3/min; (B) with feed of 25% C$_2$H$_2$/65% H$_2$/2% CO/8% N$_2$ with the same total flow.

200 mg samples of the Ni/SiO$_2$ catalyst were held in a 6 mm I.D. Pyrex reactor mounted vertically. Liquid products were collected in a lower receiver cooled to 0 °C. Samples of the liquid accumulated over the period of reaction were analysed by GC–MS and by FID–GC using identical Rtx-1 capillary columns programmed at the same rate. The identity of compounds responsible for particular peaks were established by measurements of elusion orders relative to it in extensive literature tabulations of Kovats indices for the same type of column [12]. The identity of two isomers of particular interest, cis- and trans-3-methyl-1,3-pentadiene, was also verified by matching product chromatograms against that of a mixture of the two isomers, the composition of which was established by proton NMR [12]. Gases passing through the ice trap were analysed on line with two additional chromatographs, one for C$_1$, C$_2$ and iso-C$_4$ compounds, the other for individual C$_1$, C$_2$, C$_3$ and C$_4$ compounds plus C$_5$ and C$_6$+ components as partially resolved envelopes.

The Ni/SiO$_2$ catalysts were made in batches of 5 g by incipient wetness impregnation of silica gel (Davison grade 62, surface area 285 m^2/g, particle size 75–250 μm) using a solution of Ni(NO$_3$)$_2$ of concentration such that the final Ni content of the catalyst was 2.0 wt%. After drying, each batch of catalyst was calcined in air. The 200 mg samples to be tested were then reduced in the reactor according to a set program that ended with 3 h in pure hydrogen at 450 °C. In some experiments, 200 mg samples of 2 wt% Pt/SiO$_2$ made similarly, were located below the Ni/SiO$_2$ and were co-reduced in the reactor at the same time.

The standard feed stream comprised 25% C$_2$H$_2$, 65–75% H$_2$, 0–10% CO, with N$_2$ as the balance gas as needed. The mixtures were made up using separate mass flow controllers arranged to give a total flow rate of 50 cm^3/min. The acetylene was instrument grade containing <2 ppm of PH$_3$, H$_2$S and NH$_3$ taken together. It also contained some acetone, which passed over the Ni/SiO$_2$ without reaction but was hydrogenated on Pt/SiO$_2$ (if present) to the extent noted previously [12]. One-off experiments were also carried out using a less pure grade of acetylene known to contain much higher concentrations of phosphine as explained in Section 3.2.

3. Results

3.1. Catalyst characteristics and activity for CO hydrogenation

As described previously [12], the surface area of the nickel particles in the reduced samples was typically 1.1 m^2/g(catalyst) based on CO uptake measurements with an average metal particle diameter of ~9 nm (as measured by TEM and XRD), equivalent to a disper-

sion of ~10%. The XRD patterns of some reduced samples showed small quantities of NiO but it was unclear if the NiO was a consequence of incomplete reduction or of re-oxidation while exposed to air before and during the determination of the diffraction pattern.

The activity of the Ni/SiO$_2$ for hydrogenation of CO was determined using a 10% CO, 65% H$_2$, balance N$_2$ mixture at the standard flow rate of 50 cm^3/min. After 2 h of reaction, the conversion of CO over 200 mg of Ni/SiO$_2$ at 200 °C was 0.8% based on the sum of the methane and ethane produced (with selectivities of 84% and 16% respectively). The conversion is equivalent to a turnover frequency of 3.3 × 10^{-3} molecules (CO) per surface Ni atom per second. The range expected by extrapolation of literature data for low dispersion catalysts measured at temperatures from 240 to 275 °C [13–16] is 0.8 to 3 × 10^{-3}/s, calculated assuming an activation energy of 100 kJ/mol and kinetic orders of −0.4 in CO and 0.9 in H$_2$ [17,18].

3.2. The effect of carbon monoxide on deactivation during acetylene oligomerization

Preliminary tests show that the differences brought about by the presence of CO were most pronounced at a reaction temperature of 200 °C. Fig. 1 compares reaction characteristics over time when using 25% C$_2$H$_2$, 65% H$_2$ feeds with and without 2% CO. The conversion of C$_2$H$_2$ was clearly greater when CO was present and the quantity of higher products (C$_3$–C$_6$ vapors and liquids condensable at 0 °C) considerably larger. The data for the two experiments were assembled on the basis that the liquid products, collected as a single fraction over the entire period of reaction, were produced at intermediate times at rates proportional to the conversion of acetylene. The overall mole balances are quite good bearing in mind this assumption, the need to allow for the 30–50% reduction in flow rate that accompanied reaction, and the summation of more than 10 individual C$_1$–C$_4$ compounds and many more C$_5$ and C$_6$ products in unresolved envelopes. The calculations also exclude the deposition of carbonaceous matter on the catalysts (1–2% of the acetylene fed over the 300 min of reaction) that may have been deposited non-uniformly over time.
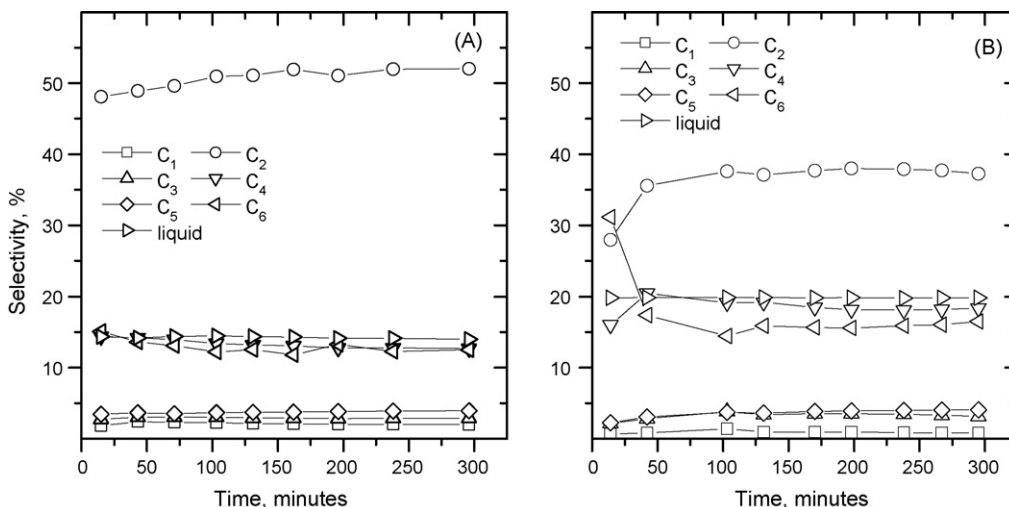
The difference in product distribution between Fig. 1A and B was not due to the contribution of products formed by the reaction of CO since, within the accuracy of the measurements, no CO reacted, and nor would methanation be expected on the basis of the tests described above. Indeed the yield of methane was less when CO was present (~0.8%) than in its absence (~1.5%). Thus the effect on product distribution must be a consequence of the influence of CO on the C$_2$H$_2$/H$_2$ reaction itself.
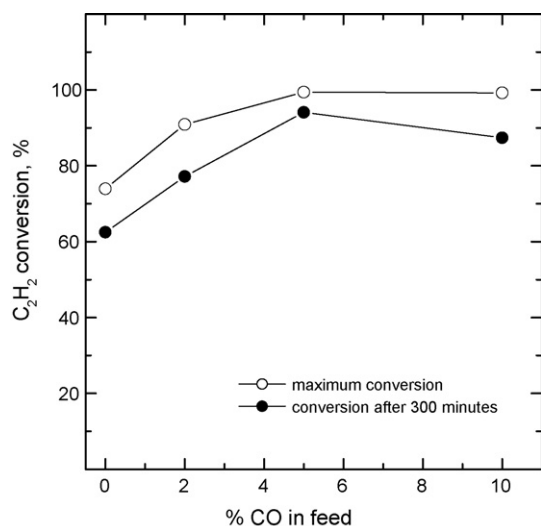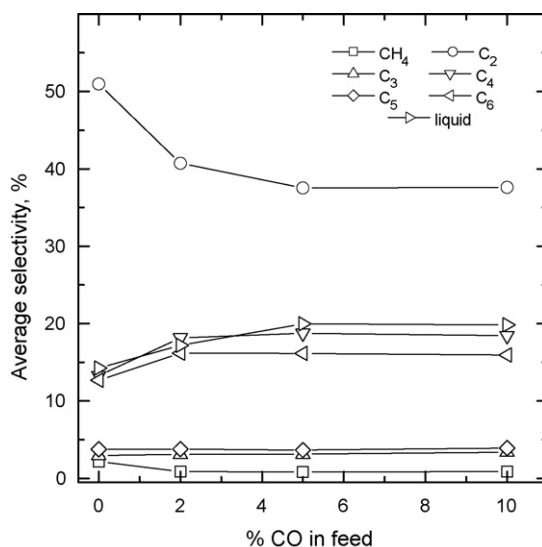
Fig. 2. Effect of carbon monoxide on maximum acetylene conversion and acetylene conversion after 300 min of reaction at 200 °C for feed comprising 25% C_2H_2/65% H_2/x% CO/$(10 - x)$% N_2 with total flow rate of 50 cm^3/min.

Experiments with other concentrations of CO at 200 °C showed that both the maximum acetylene conversion attained, and the conversion noted after 300 min of reaction increased with the CO concentrations up to 5% CO and then plateaued or declined slightly (Fig. 2). The effect of 5% CO was also tested at 150 and 170 °C. At both temperatures the conversion of C_2H_2 was complete for the standard 300 min of reaction, as found previously for reaction at 140 °C [12], and the effect of CO on catalyst deactivation could not be assessed. However the effect on product distribution was qualitatively the same as that at 200 °C, i.e. proportionally more C_4, C_6 and higher products were produced with CO present.

Unlike CO, inclusion of water (2%) had no discernible effect on the extent of acetylene hydrogenation at 200 °C. Likewise ethylene had little effect when added at the 20% level. For example, when using a 1:1:3 C_2H_2/C_2H_4/H_2 mixture, the percentage of the C_2H_2 unreacted after 300 min of reaction at 200 °C was 24% compared with 25% in a matching experiment with a 1:1:3 C_2H_2/N_2/H_2 feed. Net ethylene production [i.e. C_2H_4(in) less C_2H_4(out)] was also similar, 39% when the feed contained ethylene versus 36% when it was not, and ethane formation was also similar (6% and 5% respectively).
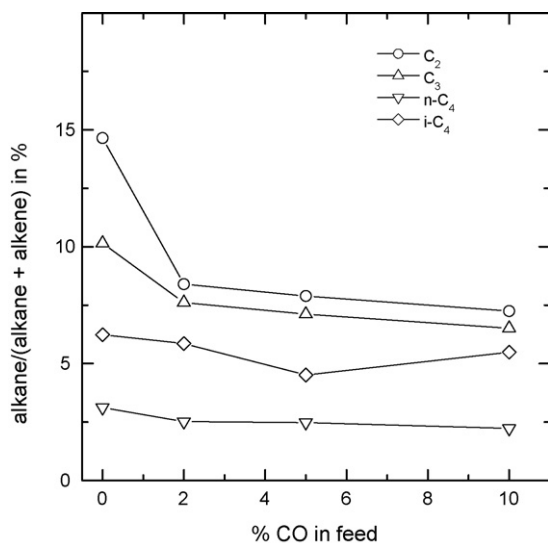

Fig. 4. Dependence of average selectivity on % CO during reaction over Ni/SiO$_2$ at 200 °C using mixtures with composition 25% C_2H_2/65% H_2/x% CO/$(10 - x)$% N_2 and a total flow rate of 50 cm^3/min.

During screening it was also found that the Ni/SiO$_2$ catalyst was sensitive to the impurities present in industrial grade acetylene. When using a welding grade acetylene, stated by the supplier to contain approximately 600 ppm PH$_3$, 10 ppm H$_2$S, 40 ppm NH$_3$ and possibly some AsH$_3$, the conversion at 150 °C fell steeply from 100% to 25% over the period between 60 and 100 min of operation and then more gradually to a plateau of 20%.

3.3. The effect of carbon monoxide on selectivity to C_1–C_4 products

Fig. 3 shows the data in Fig. 1 plotted in terms of selectivity (the percentage of acetylene converted to a particular product relative to that converted to all products). The selectivity to each product was largely independent of time from 100 min of reaction onwards despite considerable changes in C_2H_2 conversion. Given this relative constancy, the intrinsic effect of CO on product distribution was conveniently assessed in terms of the conversion averaged over the period from 100 to 300 min of reaction. As shown in Fig. 4, the average selectivity to C_2 products (ethane + ethylene) fell from just over

Fig. 3. Selectivity versus time on stream for reaction over Ni/SiO$_2$ at 200 °C in the absence and presence of 2% CO. (A) With feed comprising 25% C_2H_2/65% H_2/10% N_2 with total flow rate of 50 cm^3/min; (B) with feed of 25% C_2H_2/65% H_2/2% CO/8% N_2 with the same total flow.

Fig. 5. Effect of % CO on alkane production for C_2–C_4 products of the reaction of 25% C_2H_2/65% H_2/x% CO/$(10 - x)$% N_2 mixtures over Ni/SiO$_2$ at 200 °C with total flow rate of 50 cm^3/min.

Fig. 6. Full range chromatograms of the liquids produced by reaction at 200 °C. (A) With feed comprising 25% C_2H_2/65% H_2/10% N_2 with total flow rate of 50 cm^3/min; (B) with feed of 25% C_2H_2/65% H_2/2% CO/8% N_2 with the same total flow.
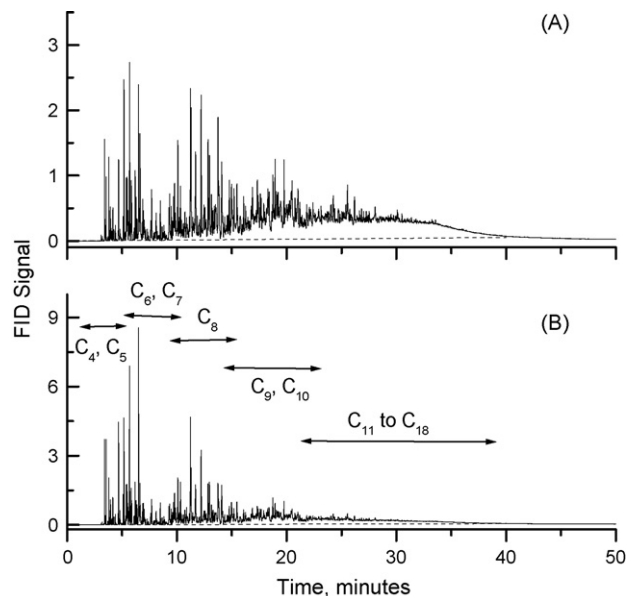
50% in the absence of CO to ∼38% with 10% CO in the feed, with most of the change already apparent when 2% CO was present. Conversely the selectivities to C_4, C_6 and liquid products all increased from less than 15% to between 16% and 20%. Selectivities to the minor C_3 and C_5 products showed little change, consistent with the conclusion that CO was not incorporated to make hydrocarbons, but that to methane almost halved.

In addition to affecting the overall product selectivity in the above ways, CO had a clear effect on the alkane to alkene ratio as shown in Fig. 5. The percentage of ethane relative to ethane + ethylene taken together fell from 15% in the absence of CO to 7% when 10% CO was present. The yield of alkane was also lower for C_3 and C_4 products but the fall-off with increasing percentage of CO was less pronounced.

Irrespective of CO concentration, the distribution within C_4 products was always highly olefinic and far from equilibrium. For the experiments on which Figs. 4 and 5 are based, the composition of this fraction with 2%, 5% and 10% CO present was 1-butene $\cong$37%, cis-2-butene also $\cong$37%, isobutene $\cong$12%, trans-2-butene $\cong$7%, 1,3-butadiene $\cong$7%, n-butane $\cong$2% and isobutane <0.5%. The selectivity to 1-butene was somewhat higher (46%), and that to cis-2-butene was correspondingly lower (24%), in the absence of CO.

3.4. Effect of carbon monoxide on the composition of the liquid fraction

Fig. 6 compares the flame ionization detector (FID) chromatogram of the liquid collected at 0 °C during the experiment carried out in the absence of CO with that obtained when 2% CO was present in the feed. Clearly CO caused an increase in the inten-

sities of peaks due to C_6 products relative to those for C_8 products. A reduction in the extended envelope of C_{11}–C_{18} is equally obvious. The chromatograms of liquids produced by experiments with 5% and 10% CO presence were qualitatively similar to that in Fig. 6B.

Integration of the chromatograms to obtain the product distribution by carbon number was inevitably somewhat arbitrary due to overlaps in the retention times of molecules with different carbon numbers and small drifts in baseline during elution. Table 1 shows the relative amounts calculated using the best compromise for retention time cut-offs. Note that the fraction denoted "C_8" actually includes toluene, which eluted with a retention time (∼10.1 min) that was longer than those for some low-boiling branched octenes that were formed in small amounts and eluted earlier than 10 min. The "C_8" fraction also includes a small number of branched nonenes that eluted before p-xylene. Similarly the "$C_9 + C_{10}$" fraction may include some low boiling branched C_{11} alkenes, and the "C_{11}+" fraction some high boiling C_{10} polyenes and aromatics. The data show, in general terms, that CO doubles the amounts of the $C_6 + C_7$ fraction, and increases that of the "C_8" fraction to a lesser extent, with a corresponding decrease in "C_{11}+" material—but the trend is rather irregular due to the uncertainties in integration.

Carbon monoxide also altered the distribution between individual products with the same carbon number as shown in Fig. 7 for C_6 compounds identified with certainty by GC–MS and other means as described in Section 2 and reference [12]. For reasons of clarity, the naming of compounds on the figure has been restricted to the major products. The names of other numbered products are given in the legend and a list identifying more minor products can be

Table 1
Effect of CO on carbon number distribution (in %) for liquid products.[a]

Retention time range (min)	Carbon number range	% CO in feed			
		0	2	5	10
4.65–9.24	$C_6 + C_7$	8	17	14	20
9.24–16.02	"C_8"[b]	21	29	25	30
16.02–21.60	"$C_9 + C_{10}$"[c]	22	21	20	21
21.60–50.00	"C_{11} +"[c]	49	34	41	29

[a] Obtained by integration of FID chromatograms of the form shown in Fig. 6 between the time limits shown.

[b] Includes toluene and branched nonenes with retention times less than that of p-xylene (16.02 min).

[c] See text for qualifications as to carbon numbers.
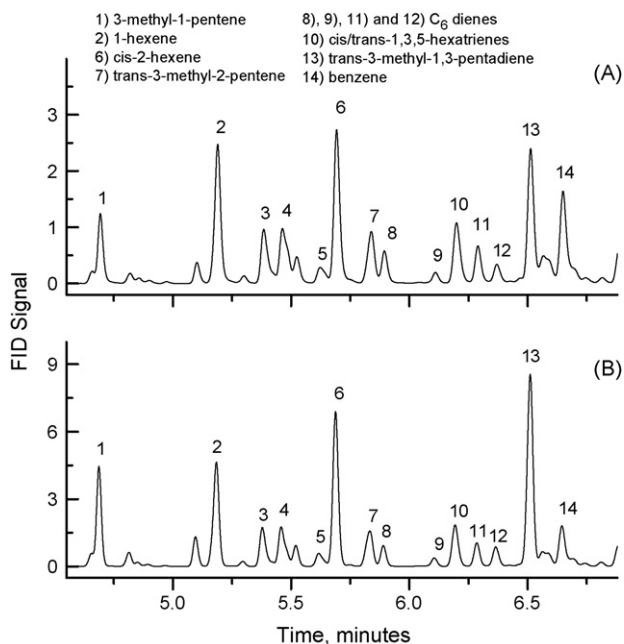
Fig. 7. C_6 regions of the chromatograms shown in Fig. 6. Minor numbered peaks as follows: (3) 2-ethyl-1-butene; (4) mixture of trans-2, cis-3 and trans-3-hexene; (5) cis-3-methyl-2-pentene; (8) cis-2-methyl-1,3-pentadiene; (9) C_6-diene; (11) 5-methyl-1,3-cyclopentadiene; (12) cis-3-methyl-1,3-pentadiene.

found in our earlier work [12]. Most significantly, carbon monoxide reduced the extent to which benzene (peak 14) was formed in relative terms, increased formation of trans-3-methyl-1,3-pentadiene (peak 13) but decreased that of 1,3,5-hexatrienes (peak 10). The tendency of CO to favour production of branched products over linear ones was also apparent amongst the principal C_6 alkenes with more 3-methyl-1-pentene (peak 1) relative to 1-hexene (peak 2) and cis-2-hexene (peak 6).

This behaviour extended to higher CO concentrations (Fig. 8) and to the product distribution within the "C_8" region (Fig. 9) where the relative amounts of toluene, ethylbenzene, styrene and the sum of the o- and m-xylene formed all fell in relative terms when 2% (or more) CO was present.
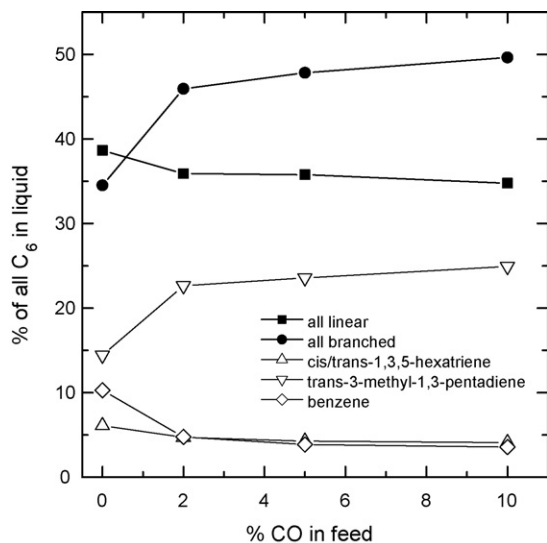
Fig. 8. Effect of CO on distribution between C_6 products in liquids formed during reaction of 25% C_2H_2/65% H_2/x% CO/$(10 - x)$% N_2 mixtures over Ni/SiO$_2$ at 200 °C. Total flow rate of 50 cm^3/min.
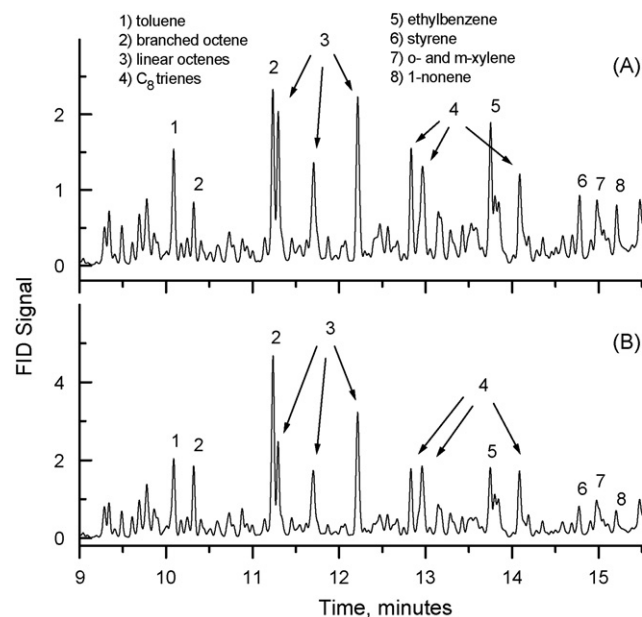

Fig. 9. C_8 regions of the chromatograms shown in Fig. 6.

3.5. Effect of carbon monoxide on subsequent hydrogenation over Pt/SiO$_2$ placed downstream

As part of our previous work it was shown that the unsaturated products produced by acetylene oligomerization over Ni/SiO$_2$ could be largely hydrogenated to alkanes at 140 °C if an equal weight of Pt/SiO$_2$ was placed immediately downstream [12]. In the absence of CO this was found also to be possible at 200 °C in the present work. As shown in Fig. 10A, n-hexane (peak a1), formed by the hydrogenation of linear C_6 alkenes and polyenes, and 3-methylpentane (peak a2), formed from their branched counterparts, were the major products. The dienes and trienes responsible for peaks 8–13 in the chromatogram of the product from oligomerization over Ni/SiO$_2$ alone (Fig. 7A) were removed completely.

The extent of hydrogenation over Pt/SiO$_2$ was much less when the feed contained 5% CO (Fig. 10B). The polyenes formed over Ni/SiO$_2$ alone (Fig. 7B) were still largely hydrogenated,
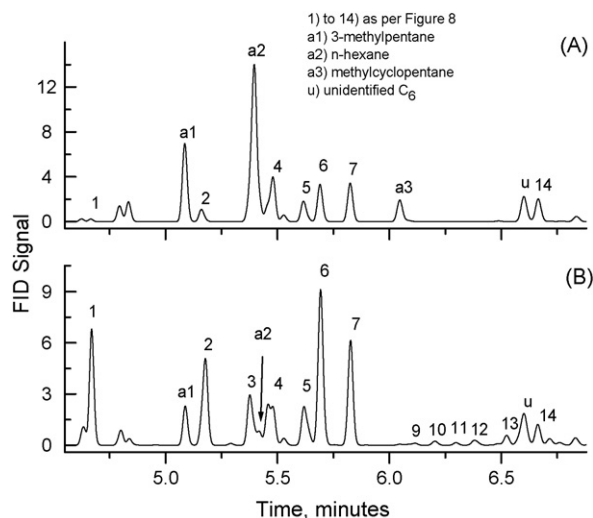
Fig. 10. Effect of CO on the C_6 region of chromatograms of liquids formed during reaction over 200 mg Ni/SiO$_2$ with 200 mg of 2% Pt/SiO$_2$ downstream at 200 °C. (A) When using a feed comprising 25% C_2H_2/75% H_2 with a total flow rate of 50 cm^3/min; (B) when using a feed comprising 25% C_2H_2/70% H_2/5% CO at the same total flow.

although traces did remain, but production of alkanes was almost non-existent. The alkenes increased to the largest amount by hydrogenation were trans- and cis-3-methyl-2-pentene (peaks 7 and 5), formed by the hydrogenation of the corresponding dienes (peaks 13 and 12 respectively), and 1-hexene (peak 6) from linear hexadienes and trienes. The same pattern was apparent for higher products (not shown). In the absence of CO, the C_8 alkenes and trienes formed during oligomerization over Ni/SiO_2 alone (Fig. 9A) were largely hydrogenated to alkanes, the most important of which were 3-methylheptane, 3-ethylhexane and *n*-octane as found previously [12]. With CO present only polyenes (peaks denoted by 4 in Fig. 9B) were hydrogenated and then only as far the corresponding alkenes (numbered 2 and 3).
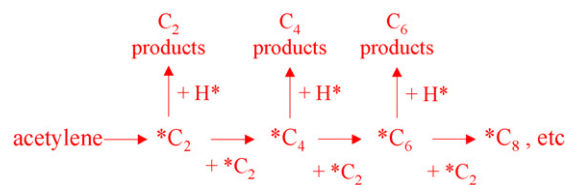
The absence of hydrogenation of alkenes to alkanes in the presence of CO is to be expected given the many definitive studies showing that CO is a very strong inhibitor of ethylene hydrogenation over Pt, both silica-supported and as single crystals [19–23].

4. Discussion

Under the conditions employed here, the inclusion of carbon monoxide aided the conversion of acetylene to oligomers in two ways. It allowed higher conversion (Fig. 2) and increased the yields of useful fractions (Fig. 1). As shown in Table 2, calculated by combination of data for gaseous and liquid products, the selectivity to LPG ($C_3 + C_4$) was raised from 16% to 22% and that of the gasoline fraction ($C_5–C_{10}$) from 24% to 34%. These increases occurred almost entirely at the expense of hydrogenation to C_2 products, since formation of diesel components ($C_{11}+$) was little changed.

The increase in oligomerization can be explained in the following way. Acetylene adsorbs molecularly on bare nickel surfaces at low temperature [24–29] but dissociates readily to form ethynyl (HCC—) and/or methylidyne (H—C≡) species at or below room temperature and then carbon at still higher temperature [30–34]. The initial heat of adsorption to form the dissociated species is in the range 190–250 kJ/mol [35,36]. The heat of adsorption of the molecular species has not been measured but calculations give values in the range 180–285 kJ/mol [37–40]. By contrast the dissociative adsorption of H_2 on nickel has a heat of 80 kJ/mol [41,42]. While binding energies may be substantially lower at the high coverages present during hydrogenation the difference in bond strength will remain. Thus under hydrogenation conditions using C_2H_2 and H_2 alone, the nickel surface should be largely covered by acetylene and its fragments together with other spectator species such as ethylidyne (CH₃C≡) and vinylidene (H₂C=C—), as described in recent DFT studies of the Pt(1 1 1) and Pd(1 1 1) systems [43,44]. Adsorption of H_2 should be restricted to gaps between the more strongly bound hydrocarbon species.

The initial heat of adsorption of carbon monoxide on nickel is ∼130 kJ/mol [41,42,45,46] which infers that it is not expected to displace acetylene but should adsorb in preference to H_2. Thus H_2 dissociation should be inhibited, and the availability of surface

Table 2
Effect of CO on overall selectivity (in %) for gaseous and liquid products combined.[a]

Fraction	% CO in feed				
	0	0.5	2	5	10
CH_4	2.2	1.0	0.9	0.8	0.9
C_2	51	47	41	37	38
$C_3 + C_4$	16	22	21	22	22
$C_5–C_{10}$	24	26	31	32	34
$C_{11}+$	7	5	6	8	6

[a] As % of acetylene reacted. Calculated by combination of data for the distribution within liquid fractions alone (Table 1) with that for the overall distribution (such as that shown in Fig. 1).

Scheme 1.

hydrogen atoms is less, when CO is present. Inhibition of H_2 dissociation by CO in the absence of acetylene is well established for Ni/SiO_2 from H_2/D_2 exchange measurements [47].

If less surface hydrogen is available, and oligomerization follows a chain growth mechanism as found previously [12], then the probability of termination of surface $^*C_2$ or higher $^*C_{2n}$ intermediates (hydrogen content omitted) to form the corresponding C_2 or C_{2n} gaseous products should be reduced relative to that of chain propagation to the next highest surface intermediate $^*C_{2n+2}$. This will favour production of higher molecular weight products as observed. Likewise, if the surface hydrogen concentration is lower then one would expect a lesser extent of hydrogenation of alkenes to alkanes, in agreement with the data in Fig. 5 (Scheme 1).

Although the presence of CO increased the yield of oligomers from C_4 to C_{10} (Table 2), the effect did not persist to still higher carbon numbers. Indeed, as is clearly evident from the chromatograms in Fig. 6, the product spectrum is distinctly truncated above C_{10}. There are two possible explanations. One is that the additional crowding introduced by the adsorption of CO at gaps between hydrocarbon species hinders the growth of long chains. While various ways by which this might occur can be envisaged, we know of no literature data to support the proposition. An alternative possibility is that the lower surface hydrogen concentration with CO present leads to an increase in multiple unsaturation, and hence to greater reactivity amongst larger molecules, resulting in condensation to products that are deposited on the catalyst as carbonaceous matter. Such loss to the catalyst would truncate the distribution in the liquid fraction as observed.
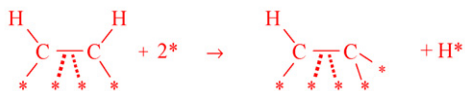
There is experimental support for this idea. As noted in Section 3.2, some acetylene was lost as carbonaceous deposits on the catalysts. While the proportion was small in terms of the acetylene fed (1–2%) it was substantial relative to the weight of catalyst and varied with the CO content. In the absence of CO the weight gain over 5 h of reaction was typically 20% (i.e. ten times the weight of Ni present). This gain is in line with the microbalance data of Guimon et al. [48] that showed a gain of 0.2 mg (coke)/mg(catalyst) over 3 h of reaction at 175 °C using a 15% C_2H_2/60% H_2 feed. In our experiments the weight gain was considerably greater with CO present—approximately 40% over 5 h when the feed contained 10% CO. Indeed the increase to mass was visibly obvious. Over the course of reaction, the catalyst bed grew in length by an amount commensurate with the gain in weight.

Given the larger amount of deposited material it is somewhat surprising that inclusion of CO did not induce deactivation but conferred higher conversion, both initially and over the course of reaction (Figs. 1 and 2). The implication is that this type of deposited material is located on the support or in some other form that does not block reaction sites on the nickel surface. The origin of the beneficial effect of CO on overall conversion is not obvious but one possible explanation is as follows. The $C_2H_2 + H_2$ reaction as studied here is somewhat unusual in that the conversion, both initially and over time, is lower at higher temperatures [12]. This is possible if the activation energies of reactions producing deactivating species are higher than that of the reaction itself. Methylidyne and carbidic carbon, the most stable decomposition products of acetylene, are possible deactivating species. The path to such species on nickel surfaces is not certain but on Ni(1 0 0) the dissociation appears to be

Scheme 2.

sequential, acetylene to ethynyl (−CCH) to methylidyne and carbon [34], as also indicated by calculations for a Rh(1 0 0) surface [49]. Formation of ethynyl can be represented in the following way with the surface species depicted in di−σ/di−π form as is the case for the adsorption of acetylene on a Ni(1 1 1) surface [26] (Scheme 2).

The dissociation of adsorbed acetylene to form the ethynyl species requires transfer of H to an adjacent vacant site (*) and hence would be hindered by co-adsorbed CO. In this way carbon monoxide could hinder acetylene dissociation and hence the production of deactivating species. The lesser amount of CH_4 formed under steady state conditions, 0.8% with CO present versus 1.5% in its absence (Fig. 3), is consistent with this interpretation.

The inhibition of C_2H_2 dissociation by CO should be particularly effective when the pretreated catalysts containing bare nickel surfaces are first contacted with the reaction mixture. The initial sticking probabilities for C_2H_2 and CO are similar (each 0.7–0.8 [35,36,45]) so some of the C_2H_2 first adsorbed will have adsorbed CO as instantaneous nearest neighbours and this will lessen the probability of dissociation to form carbon on active sites. The higher initial activity for acetylene oligomerization with CO present may be a consequence of this effect.

The above explanations for the twin effects of CO, higher activity overall and a favouring of LPG and gasoline fractions, are linked. In both cases CO competes for surface sites that can accept hydrogen atoms, in the first instance from acetylene, in the second from molecular hydrogen dissociation. The explanation is also consistent with the data of Jackson and Hodgson [50] for the co-adsorption of CO and propyne on Ni/Al$_2$O$_3$ at 300 °C. Adsorption of CO was strongly suppressed by propyne. Even so, CO restricted the formation of methane through the decomposition of propyne favouring self-hydrogenation to propene and the continued deposition of carbonaceous material in amounts that greatly exceeded the nickel surface area and were thought to have migrated to the support.

The incomplete deactivation caused by impurities in welding grade acetylene is likely to be caused by the conversion of Ni particles to Ni$_2$P given the work of Yang et al. [51] which shows that phosphine, the principle impurity present, reacts readily with Ni at 150 °C and above. The retention of some activity by the phosphided catalyst is not surprising given reports that amorphous nickel–phosphorus alloys have considerable activity for the selective hydrogenation of acetylene [52,53].

5. Conclusions

Although carbon monoxide does not participate directly in acetylene oligomerization over Ni/SiO$_2$, its presence has two beneficial effects. It improves the conversion, both initially and over time, and improves the selectivity to useful LPG and gasoline range products over C$_2$ products. However the favouring of oligomer production is not apparent above C$_{10}$. Methane and higher alkanes are always minor products and carbon monoxide increases the dominance by alkenes amongst C$_2$–C$_4$ products while lowering methane further. Carbon monoxide also alters the distribution of products in condensable material. Amongst C$_6$ products, it favours branched products over linear ones and dienes relative to alkenes while disfavouring benzene (and also higher aromatics). The major benefits of CO can be explained by current knowledge concerning adsorption on nickel surfaces on the basis that carbon monoxide competes for adsorption sites that would otherwise be available to accept

hydrogen atoms derived by the dissociation of hydrogen or acetylene. If the concentration of hydrogen atoms at the surface is lower, then propagation of surface species should be favoured relative to termination to gaseous products. If acetylene dissociation is disfavoured then less surface carbon will ensue and activity should be higher as a result. The truncation of production of oligomers greater than C$_{10}$ is most likely a reflection of the condensation of highly unsaturated products to carbonaceous material on the support given that the gain in catalyst weight during reaction is higher when carbon monoxide is present.

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