

Homologation reactions of alkanes on transition-metal surfaces

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HOMOLOGATION REACTIONS OF ALKANES ON TRANSITION-METAL SURFACES

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Abstract

A combination of experiments using TAP, and isotopic labelling of hydrocarbons using ^{13}C over metal catalysts has provided useful information about the formation of carbon surface species and their activity. The formation of non-reactive surface species following high temperature CO or CH_4 adsorption was shown to be more likely at high temperatures, and that this was a fairly rapid process. The activation energy for C-C coupling reactions was found to be higher following promotion of a Ru catalyst with V. Differences in *n*-*iso*-ratio between labelled and non-labelled products indicated that different reaction pathways led to the formation of *n*-hexane and *iso*-hexane.

INTRODUCTION

Work by Koerts *et al.*¹ showed that carbon atoms from $^{13}\text{CH}_4$ could be inserted into ethylene or propylene in a surface reaction carried out on supported Co and Ru catalysts. Due to the thermodynamics, this reaction cannot be carried out in one step, and so a procedure was developed where the CH_4 activation step was separated from the associative carbon insertion step¹. Figure 1 illustrates the devised reaction scheme. A CH_4/He stream was passed over the Ru catalyst at 450 °C, resulting in the formation of dehydrogenated surface CH_x species. The catalyst was then cooled rapidly in He to 50 °C at which point pulses of ethylene were passed over the metal surface. This resulted in the formation of several types of dehydrogenated surface species, including C_3H_y . These species could be hydrogenated at 50 °C resulting in the formation of propane. The use of ^{13}C in these experiments provided important mechanistic information about the formation of longer alkanes via C-C bond formation.

TPR and IR-spectroscopy studies have proven the existence of different types of

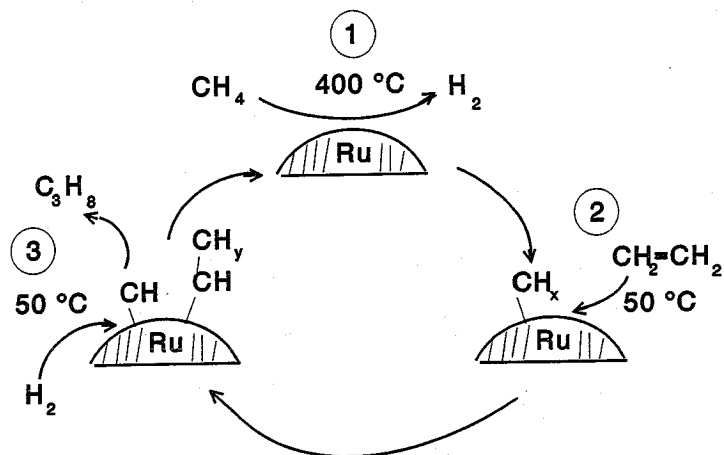


Figure 1. Reaction cycle for the stepwise conversion of methane and an olefin to a higher homologue¹.

adsorbed carbon species following the dissociation of CH₄ or CO over metals such as Ru or Co, and the species formed from CO have been shown to have a higher methanation activity than the non-dissociated molecule. The activity of species formed from CO dissociation has been found to be similar to that from methane decomposition on transition metals between 350 °C and 550 °C^{2,3}. It is generally recognised that there are three types of surface carbon species formed, and these are usually referred to as C_α, C_β and C_γ. C_α is usually thought to be carbidic in nature and formed at low temperatures⁴⁻⁶, and can be hydrogenated to form methane at temperatures ≤50 °C. Calculations have shown this carbon to be adsorbed in hollow sites bounded to three or more surface metal atoms⁷. A less reactive surface carbon type, usually referred to as C_β, can be hydrogenated at temperatures between 100 °C and 300 °C, and has been described as being amorphous in nature^{8,9}. Carbon deposited at higher temperatures via methane or CO dissociation is characterized as being graphitic in nature, C_γ. Once deposited it is believed that the carbidic carbon can be converted to the graphitic form by heating, however this transformation is generally regarded as being irreversible. It has been shown³ that only the C_α species have reasonable selectivities for the production of higher hydrocarbons. Recently we have carried out experiments using the TAP¹⁰ apparatus here in Eindhoven to study in more detail the nature of the carbon species formed on transition metals as a result of high temperature CO and methane treatment. Further evidence has been obtained for the formation of non-reactive surface species at high temperatures, and we have observed that this process can be fairly rapid.

We have recently used a procedure similar to the two-step reaction described above for the production of ¹¹C-labelled *n*-hexane from ¹¹CO and 1-pentene over supported Ru catalysts¹¹. The production of labelled *n*-hexane is part of a larger project where *n*-hexane isomerization over zeolite catalysts will be studied using Positron Emission Profiling (PEP); a similar technique has been used previously for the study of CO oxidation over automotive exhaust catalysts^{12,13}. Over Ru, a C_{*n*} olefin can undergo cleavage, mainly at the terminal bond position. It has been shown that the resulting C₁ surface species can recombine with the alkene to produce C_{*n*+1} alkanes¹⁴. The incorporation of ¹¹C into the reaction products therefore allows one to distinguish this self-homologation process from that involving the reaction of a surface C₅ species with a C₁ species produced from high-temperature CO adsorption. Differences in the *n*-/*iso*- product ratios between labelled and non-labelled products also gave information about the pathway for *n*- and *iso*-product formation.

TAP EXPERIMENTS

Experimental

Three catalysts: 5%Ru/SiO₂, 5%Pt/SiO₂ and 4.5%Rh/SiO₂ were prepared in this laboratory using incipient wetness impregnation of Grace silica 332 with aqueous solutions of the appropriate metal salts. A fourth catalyst, 2.3%Pt-2.7%Rh/SiO₂, was supplied for us by a group in Germany¹⁵.

For each experiment approximately 50 mg of catalyst was placed in the centre section of the TAP micro-reactor. On either side of the catalyst bed the reactor was filled with inert Grace silica. Two types of experiment were carried out using the TAP apparatus: multi-pulse, and pump-probe. In the case of multi-pulse experiments, many pulses of CO (typically about 1×10^{-7} mol per pulse) were passed over a pre-reduced catalyst. Product analysis by a mass spectrometer in the analysis chamber of the TAP equipment provided information on the CO adsorption process, and surface reactions to produce CO₂. Usually multi-pulse experiments were used to deposit a large quantity of reactive species on the catalyst surface. Pump-probe experiments involved a short single pulse of CO followed 3 seconds later by a single pulse of H₂ of similar size. From this it was possible to obtain information about product formation and the production of non-reactive surface species over relatively short time intervals. During each experiment this pump-probe cycle was repeated several times for better accuracy. Using these experiments the quantity of non-reactive carbon with respect to the CO adsorption temperature was measured over Ru, and a comparison of the reactivity of methane-produced surface C₁ towards ethane production was made between Ru, Pt and Pt-Rh. Finally, a comparison was made between the reactivity of Ru and Rh for methane formation from CO adsorption.

Results and discussion

The reaction of CO and H₂ over Ru resulted in the formation of CO₂ and methane. At lower temperatures CO adsorption was indicated by a low CO signal. At these temperatures it was observed that the production of CO₂ and CH₄ was not great. It can be assumed therefore that at temperatures of ≤ 250 °C CO is adsorbed on the Ru catalyst without dissociation. At higher reaction temperatures an increased production of both CO₂ and CH₄

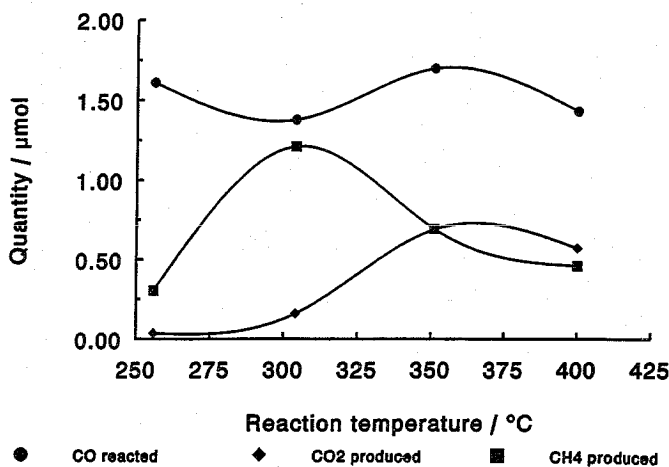


Figure 2. Carbon species produced at various reaction temperatures over 5%Ru/SiO₂

was observed. The production of CO_2 is a result of the Boudouard reaction whereby surface C_1 species are also produced^{16,17}. The formation of CH_4 at these higher temperatures therefore indicates that C_1 surface species must be reactive intermediates in this reaction rather than non-dissociated adsorbed CO. At reaction temperatures above about 310 °C a sharp reduction was observed in the CH_4 production although the quantity of CO adsorbed was found to be almost independent of temperature. This indicated that at these temperatures a large quantity of non-reactive surface carbon species was formed following CO adsorption. The quantity of CO reacted, and, CO_2 and CH_4 produced over Ru at four different reaction temperatures is illustrated in figure 2. The quantity of non-reactive carbon (C_γ) remaining on the surface can be calculated by carrying out a carbon mass-balance (1) and (2):

$$n_{\text{C}, \text{in}} = n_{\text{CO}, \text{in}} \quad (1)$$

$$n_{\text{C}, \text{out}} = n_{\text{CO}, \text{out}} + n_{\text{CH}_4, \text{out}} + n_{\text{CO}_2, \text{out}} \quad (2)$$

where: $n_{i, \text{in}}$ = the number of moles of component i at the reactor inlet
 $n_{i, \text{out}}$ = the number of moles of component i at the reactor outlet

The percentage of carbon which remains on the catalyst as a non-reactive species (C_γ) is then given by (3):

$$\% \text{C}_\gamma = \frac{n_{\text{C}, \text{out}} - n_{\text{C}, \text{in}}}{n_{\text{C}, \text{in}}} \times 100\% \quad (3)$$

At low temperatures it is assumed that no C_γ is formed as there is no evidence for CO dissociation below 250 °C. It is assumed that the deficit in the carbon mass-balance at low temperatures comes as a result of adsorbed molecular CO. The percentage carbon remaining as non-reactive species at various temperatures is illustrated in figure 3.

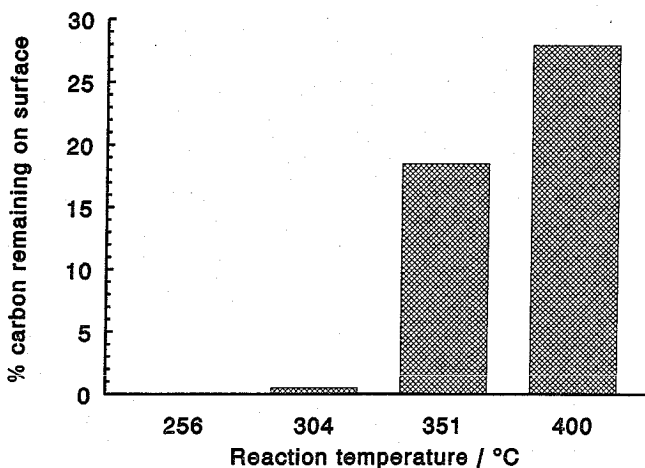


Figure 3. % carbon remaining on Ru surface as non-reactive C_γ

When the time between the CO pulse and the subsequent H_2 probe-pulse was short (3-5 seconds) the production of non-reactive surface carbon was still observed, indicating that its formation is an extremely rapid process. Evidence for the formation of these surface species has also been obtained for Rh. Over both Ru and Rh it is found that there is a

decrease in the conversion of CO to methane with increasing temperature, this is illustrated in figure 4. At all temperatures studied however, the conversion of CO to methane is higher over the Ru catalyst than over the Rh catalyst. This seems logical as Ru is the better of the two metals for CO dissociation.

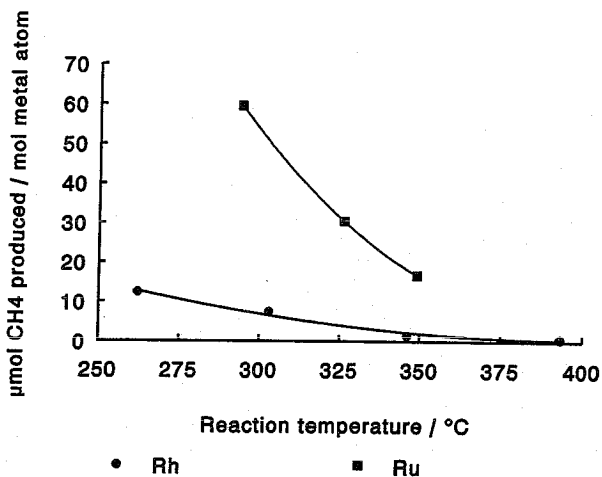


Figure 4. Quantity of methane produced per metal atom following CO adsorption over Ru and Rh

The formation of higher hydrocarbons (namely ethane), from C_1 produced from methane, was also studied. Results of pump-probe experiments carried out at 250 °C are given in table 1, where the reactant was methane, and the probe-pulse gas was hydrogen. All the results were normalised with respect to the number of metal atoms present in each catalyst sample, as the three catalysts had different metal loadings. Of the three catalysts studied (Ru, Pt-Rh and Pt), Pt was found to be the best metal for C-C coupling, Pt-Rh was found to have only about 50% of the activity of the pure Pt catalyst, and no C-C coupling reaction was observed over Ru. In the case of Ru this does not mean that C-C coupling does not take place, but just that with the quantity of reactant used, the product yield is below the detectable threshold. The effluent gas from the reactor was also checked for higher hydrocarbons, e.g. propane or butane, however with such small quantities of reactants used there was no evidence for the formation of these products.

Table 1. Ethane production following a single pulse of CH_4 (5.05×10^{-8} mol) and a subsequent single H_2 pulse (4.0×10^{-8} mol) over Ru, Pt-Rh and Pt catalysts.

Catalyst	$\mu\text{mol } C_2H_6 \text{ produced / mol metal atom}$
5%Ru/SiO ₂	-
2.3%Pt-2.7%Rh/SiO ₂	1.03
5%Pt/SiO ₂	2.13

The results of the TAP experiments show clearly that the formation of non-reactive carbon species does occur to a greater extent at elevated temperatures. Based upon a significant yield of CO_2 , and little non-reactive surface-carbon formation, it is found that the optimum temperature for CO adsorption over Ru for reactive surface-carbon production

is 300 °C. The TAP experiments also demonstrate that of the three metals Pt, Rh and Ru, Pt is the most active for C-C coupling when C₁ species have been formed via CH₄ adsorption. However as Pt is inactive for CO dissociation, this is a poor choice of metal for the formation of labelled *n*-hexane via ¹¹CO and 1-pentane. On the bases of the TAP experiments alone, the Ru and Ru-Rh are more likely to be of use for the labelling experiments as both can dissociate CO and form hydrocarbons (methane or ethane) from surface carbon species.

LABELLED *n*-HEXANE PRODUCTION

Experimental

For the production of ¹¹C-labelled *n*-hexane two sorts of catalyst have been used: a pure Ru/SiO₂ catalyst and Ru catalysts promoted with V. In all, three catalysts have been used for this work, all of which were produced in this laboratory via incipient wetness impregnation of Grace silica with aqueous solutions of the metal salts. The catalysts studied were 5.0%Ru/SiO₂, 5.3%Ru-0.7%V/SiO₂ and 5.3%Ru-1.4%v/SiO₂. The experimental set-up consisted of a quartz micro reactor, approximately 6 ml in volume, and containing approximately 400 mg of catalyst. During experiments He was continuously passed over the catalyst sample. The introduction of He and H₂ to the system was controlled by 24-volt solenoid valves, and the gas flow rates were controlled by Brooks 5850TR thermal mass-flow controllers. Non-labelled carbon monoxide could be introduced to the system via an electrically operated six-way valve (Valco Instrument Company), fitted with a 1 μmol injection loop. 1-pentene was introduced in a similar manner via a saturator operated at 21 °C. ¹¹C-labelled carbon monoxide could be introduced to the catalyst via a second electrically operated six-way valve. Products of the hydrocarbon reaction were separated by an on-line gas chromatograph (Packard model 427) fitted with a TCD and a 2 m squalane/alumina column operated at 70 °C. Labelled compounds could also be detected by the use of NaI scintillation crystals connected to photo-multiplier tubes. By positioning the TCD of the gas chromatograph and the NaI detectors in series it was possible to determine the quantity of both non-labelled and labelled products obtained. The set-up is illustrated in Figure 5.

¹¹C is a positron emitter with a half life of 20.39 minutes. Positrons only travel a short distance in solid material, and after being slowed down, the positron annihilates with an electron (usually in a neighbouring atom) producing two γ-photons, each of 0.511 MeV, travelling in opposite directions. ¹¹C was produced by bombarding high purity nitrogen with 12 MeV protons accelerated in the Eindhoven University cyclotron. A 25 minute irradiation period of 3.5 l of target gas resulted in the production of 300 MBq of activity; this is equivalent to slightly less than 1 pmol of ¹¹C. Trace impurities of oxygen present in the target vessel were sufficient to convert all ¹¹C produced to ¹¹CO₂. The ¹¹CO₂ was converted with 100% selectivity to ¹¹CO over metallic zinc granules at 390 °C. This was confirmed by ¹¹CO/¹¹CO₂ separation using a Chromosorb 102 column.

The reaction procedure for labelled *n*-hexane production was similar to that described in the introduction for the production of propane from methane and ethylene. ¹¹CO was dissociated at high temperature (300 °C - 400 °C), the catalyst was then cooled rapidly to a much lower temperature (100 °C - 150 °C) where 1-pentene was adsorbed. The resulting products were then removed from the catalyst surface by a hydrogen pulse at the same temperature as the 1-pentene adsorption.

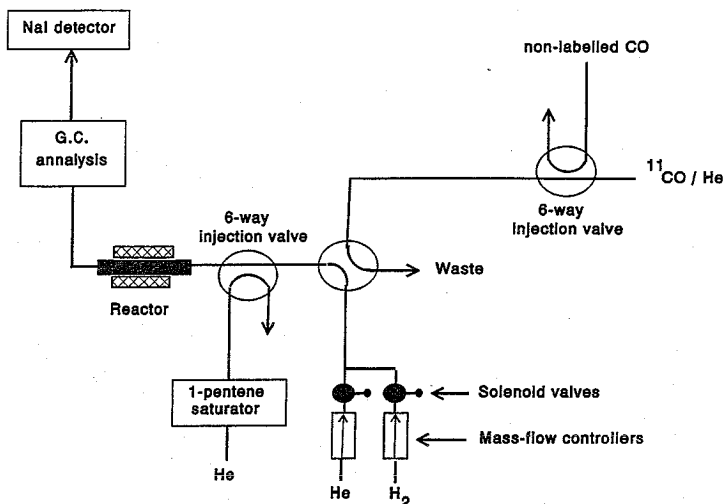


Figure 5. Simplified diagram of the set-up used for ^{11}C -labelled *n*-hexane production.

Results and discussion

On both the Ru catalyst and the V-promoted catalysts a range of labelled alkanes from C_1 to C_6 (including isomers) was produced, rather than labelled *n*-hexane alone. This came as a result of the high activity of Ru as a hydrogenolysis catalyst at the same temperatures used for product hydrogenation, i.e., ^{11}C was reacting with shorter fragments of 1-pentene. The selectivity for *n*-hexane could be defined in two ways. Firstly, the selectivity for *n*-hexane production in the product fraction isolated during the hydrogenation step (4). Secondly, this selectivity could be multiplied by the percentage of α -carbon which was formed on the catalyst, to give an overall product selectivity based on the total quantity of adsorbed ^{11}C (5). Where:

$S_{i,H}$ = selectivity for product *i* (*i* carbon atoms) during hydrogenation step

$S_{i,T}$ = total selectivity for product *i*

P_i = product *i* peak area

$X_{C\alpha}$ = fraction of labelled carbon adsorbed as the α form

Product selectivities for the hydrogenation step are given in table 2 for the three catalysts. In each case the values quoted are results where the optimum conditions were used to maximise *n*-hexane selectivity (this is discussed in greater detail below). Table 3 presents the percentage α -carbon formed on each catalyst following high temperature CO

$$S_{i,H} = \frac{P_i}{\sum_{i=1}^6 P_i} \times 100\% \quad (4)$$

$$S_{i,T} = S_{i,H} \times X_{C\alpha} \quad (5)$$

dissociation, and total *n*-hexane selectivities based on the total quantity of adsorbed ^{11}C . In no experiment was there evidence for the formation of γ -carbon. It was also found that the

β -carbon which was formed on the catalyst yielded only methane upon hydrogenation.

Table 2. Product selectivities hydrogenation at 110 °C

Catalyst	Product selectivity / %					
	methane–propane	butane	<i>iso</i> -pentane	<i>n</i> -pentane	<i>iso</i> -hexane	<i>n</i> -hexane
5%Ru/SiO ₂	69.0	3.2	0.8	7.3	3.1	16.6
5.3%Ru–0.7%V/SiO ₂	76.1	3.6	0.3	4.7	2.1	13.2
5.3%Ru–1.4%V/SiO ₂	82.6	4.2	0.7	3.5	2.7	6.3

Table 3. Fraction of adsorbed carbon in the form of C _{α} and total *n*-hexane selectivities

Catalyst	Fraction C _{α}	Total <i>n</i> -hexane % selectivity
5%Ru/SiO ₂	0.091	1.51
5.3%Ru–0.7%V/SiO ₂	0.161	2.13
5.3%Ru–1.4%V/SiO ₂	0.234	1.47

An optimum temperature for CO adsorption was observed at 325 °C where a maximum selectivity for *n*-hexane production occurred. A change in the adsorption temperature of \pm 50 °C led to a reduction in the *n*-hexane selectivity by as much as 50%. During the high temperature adsorption period the effluent gas from the reactor was analyzed and found to be mainly CO₂; at the same time a sharp increase in radioactivity was observed in the vicinity of the reactor. Both of these observations suggest that the formation of active carbon takes place via the Boudouard reaction. The influence of the CO adsorption temperature on the labelled *n*-hexane selectivity is shown in figure 6 for 5%Ru/SiO₂. A selectivity maximum was also observed in the case of the other two catalysts at about the same temperature. The selectivity maximum can be explained by thinking about the CO adsorption and dissociation process. As the adsorption temperature increases, the rate of the Boudouard reaction also increases, however the chance of CO adsorption will decrease with increasing temperature. The chance of forming non-reactive carbon also increases with temperature, and it is known that these non-reactive species do not lead to hydrocarbon production. There will therefore be a temperature where these three parameters are at an optimum to produce a maximum in *n*-hexane selectivity, and this is indeed what was found. In the case of the pure Ru catalyst it was found that it was essential to co-adsorb non-labelled CO with the labelled CO in order to adsorb a sufficient quantity of ¹¹C on the catalyst for labelled *n*-hexane production. As with the variation in CO adsorption temperature, the quantity of non-labelled CO which was co-adsorbed was also found to have a significant effect on the labelled *n*-hexane selectivity. This is illustrated in figure 7.

The non-labelled CO plays an important role in the reaction process. At low concentrations it blocks some of the Ru sites, thus reducing the hydrogenolysis activity: the chance for C-C coupling reactions therefore increases. At higher concentrations too many of the Ru sites become blocked, reducing not only the hydrogenolysis activity, but also the activity for C-C bond formation.

It was possible to calculate the activation energy for the C-C coupling reaction as the quantity of labelled *n*-hexane produced in each experiment was directly proportional to a

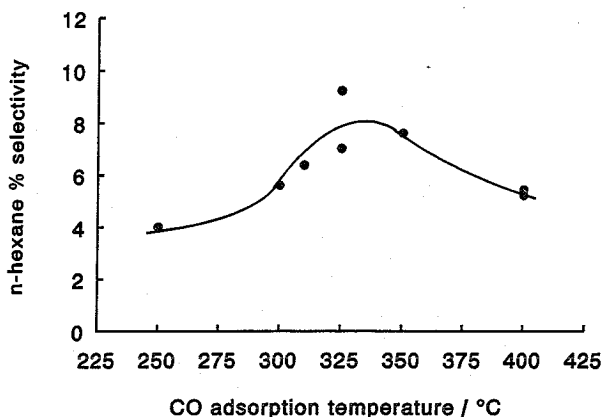


Figure 6. Influence of CO adsorption temperature on labelled *n*-hexane selectivity (5%Ru/SiO₂)

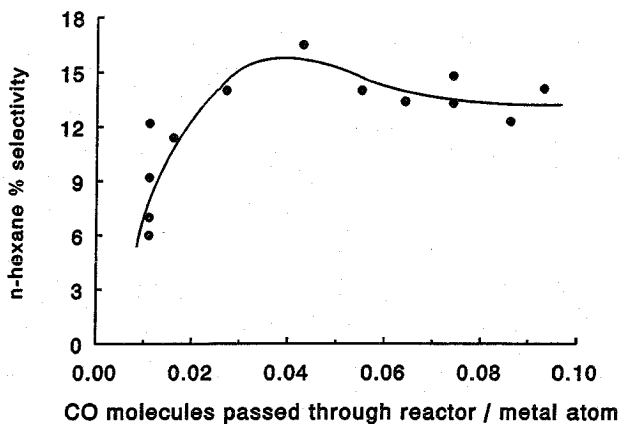


Figure 7. Influence of non-labelled CO on labelled *n*-hexane selectivity (5%Ru/SiO₂)

reaction rate. This was done for 5%Ru/SiO₂ and 5.3%Ru-0.7%V/SiO₂. Due to the small quantities of product obtained it was not possible to measure such an activation energy for *iso*-hexane formation directly from an Arrhenius-style plot, however it was noted that the *n*-/*iso*- product ratio was a useful parameter as this was also temperature dependent. From this the activation energy difference between *n*-hexane and *iso*-hexane formation could be calculated. Table 4 presents activation energies for *n*- and *iso*-hexane production over the pure Ru and the V-promoted catalyst.

It can be seen that promotion of the Ru catalyst with V raised the activation energy for hexane formation. It was observed that it was possible to use a higher 1-pentene adsorption / hydrogenation temperature in the case of the V-promoted catalyst without seriously affecting the *n*-hexane selectivity, i.e. the activation energy for the hydrogenation of all surface species from C₁ to C₆ must be increased by V promotion. The same effect was observed in earlier work where the effect of V promotion on Rh catalysts was studied¹⁸. In that study it was observed that although the activity of the surface species towards H₂ was far lower in the case of the promoted catalyst, the probability of chain growth was higher.

The conclusion was reached that the carbon species were more strongly bonded to the catalyst surface, and therefore more likely to take place in C-C coupling reactions. The results suggest that the same is true in the case of the V-promoted Ru catalysts.

Table 4. Activation energies for *n*- and *iso*-hexane formation over 5%Ru/SiO₂ and 5.3%Ru-0.7%V/SiO₂

Catalyst	Product	E _a / kJ mol ⁻¹
5%Ru/SiO ₂	<i>n</i> -hexane	40.12 ± 1.24
"	<i>iso</i> -hexane	81.02 ± 1.31
5.3%Ru-0.7%V/SiO ₂	<i>n</i> -hexane	69.63 ± 2.93
"	<i>iso</i> -hexane	120.07 ± 34.24*

At all reaction temperatures studied there was a difference observed in the *n*-*iso*-product ratio between the labelled and non-labelled product fraction. This is best illustrated in figure 8 where it can be seen that labelled *n*-*iso*-hexane ratio is approximately twice that

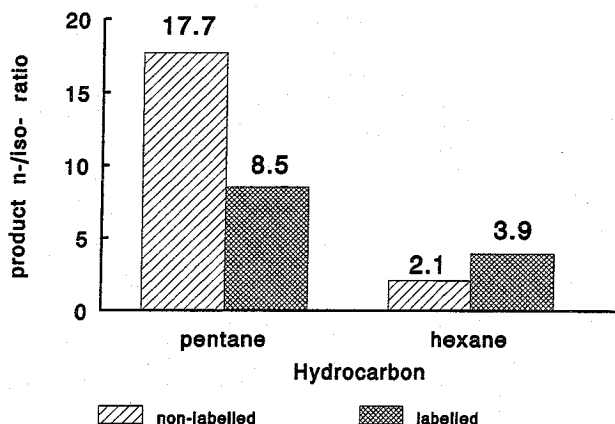


Figure 8. *n*-*iso*- ratio for labelled and non-labelled hydrocarbons hydrogenated at 110 °C. 5%Ru/SiO₂

of non-labelled hexane. This strongly suggests that C₁ addition takes place preferentially at the terminal position of the growing hydrocarbon chain, and that *iso*-alkanes are mainly formed from a reaction pathway other than C₁ addition, i.e. via the recombination of cracked pentene fragments (C₂, C₃ and C₄ species). If this was not the case one would expect the *n*-*iso*- product ratio to be the same for both labelled and non-labelled products. In figure 8 the very high non-labelled *n*-*iso*- ratio for pentane can be explained simply from hydrogenation of 1-pentene. The greater likelihood of carbon addition occurring at a terminal position has also been concluded in earlier studies¹⁹⁻²¹.

* Error in activation energy high due to the small number of data points.

CONCLUSIONS

From TAP it is clear that over metals such as Ru and Rh, the rate of formation of active surface C₁ species increases with temperature, however so does the chance of non-reactive surface carbon formation. Of the three metals Pt, Ru and Rh, TAP shows that Pt is by far the best metal for C-C coupling, however its inability to dissociate CO means that it can only be used for the production of higher hydrocarbons if CH₄ is used as the source of C₁.

From the difference in the *n*-/*iso*- ratio for labelled and non-labelled products it is clear that there are different reaction pathways leading to *n*- or *iso*- hydrocarbons. Promotion of a ruthenium catalyst with V raises the overall selectivity for *n*-hexane production. This comes about partly through an increase in the metal-carbon bond strength in the case of the promoted catalyst.

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