Metal-catalysed Alkylation of Pentene to Hexane

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The use of ^{11}C-labelled CO in the formation of ^{11}C-labelled *n*-hexane from pent-1-ene over 5% Ru/SiO_2 gives clear evidence for the presence of different reaction pathways for production of *iso*- and *n*-hexane; recombination of pentene fragments appears to be the dominant route in hexane formation.

Earlier work[1] has shown that carbon atoms from CH_4 can be inserted into ethene or propene in a surface reaction at a transition metal surface. Essential to the process was the separation of the CH_4 activation step from the associative carbon insertion step.[1] Here we report analysis of such a sequential reaction for the incorporation of C_1 species into a longer hydrocarbon chain. The focus of the investigation was the *n*/*iso*-ratio of the products.

Instead of C_1 species formed from CH_4, we produced surface C_1 species from CO. Earlier we reported the comparable reactivities of C_1 species produced from CO[2] and methane.[3] It is important to form surface carbon species from CO, as it has been shown that chain growth in Fischer–Tropsch synthesis involves partially hydrogenated surface CH_x fragments rather than undissociated CO.[4,5]

In order to distinguish C_6 formation by reaction of C_5 with surface C_1 from the recombination of C_5 fragments, one had to label the C_1 species formed from the CO. In an earlier investigation we used ^{13}C-labelled methane.[1] For the longer chain molecules the use of radiochemically labelled C_1 species is more convenient. Here we report on the use of radiochemically labelled ^{11}C, which is a positron emitting isotope. ^{11}C was produced by bombarding a gas target vessel containing high purity N_2 with 15 MeV protons accelerated in the Eindhoven University cyclotron. The ^{11}C was produced initially in the form of labelled CO_2 which was converted to CO in a Zn furnace operated at 390 °C. During the experiment described below the total activity of ^{11}C produced was 300 Mbq which was equivalent to 9×10^{-13} mol.

380 mg of a 5% Ru/SiO_2 catalyst was used in the production of ^{11}C-labelled *n*-hexane *via* the high temperature adsorption of ^{11}CO at 300 °C, and an adsorption of pent-1-ene and subsequent hydrogenation at a lower temperature of 110 °C. The overall process was similar to that used previously in the conversion of methane into higher hydrocarbons by Koerts *et al.*[2] and Belgued *et al.*[6] The catalyst was prepared by incipient wetness impregnation of Grace silica 332 (surface area 240 $m^2\ g^{-1}$) with $RuCl_3$ solution, and reduced in flowing H_2 at 450 °C prior to use. The total number of surface metal atoms was 5.6×10^{-5} mol; this was based on a 30% metal dispersion, calculated from CO adsorption measurements made at room temperature. Experimentally it was found that a quantity of non-labelled CO (2×10^{-6} mol) had to be adsorbed on the catalyst at the CO adsorption temperature prior to ^{11}CO adsorption. This may have helped to clean the surface by removal of any contaminating O atoms which may react with the ^{11}C species to produce $^{11}CO_2$. Evidence for removal of surface O from small Rh particles by CO has been observed recently by Matolín *et al.*[7] In total 8% of the ^{11}C produced (7.0×10^{-14} mol) was passed over the catalyst at 300 °C in the form of ^{11}CO.

At 110 °C, 4.1×10^{-5} mol of pent-1-ene was passed over the catalyst. This was done *via* a pentene saturator at 22 °C, and a 150 µl injection loop. The pulsing of pent-1-ene was followed by pulsing 5.4×10^{-4} mol of hydrogen over the catalyst at the same temperature. The resulting products were separated by on-line gas chromatography, and the ^{11}C-labelled hydrocarbons were detected by a NaI crystal scintillation detector. An injection loop volume of 1.2 ml was used in the GC, and in this way 11% of the hydrocarbons produced as a result of the hydrogenation step could be analysed. The total quantity of labelled hydrocarbons which were separated using the above technique was 6.4×10^{-17} mol; however this was sufficient to allow adequate resolution of each of the products. The largest errors involved in the process were in the measurement of the product-peak areas. These errors were calculated by taking into account the area of the peak and the background activity.

It was found that ^{11}C-labelled hydrocarbons were evolved from the catalyst surface in the pentene adsorption step as well as during the consecutive hydrogenation step. 4.2% of the ^{11}C adsorbed on the catalyst surface (7.5×10^{-17} mol) was removed from the catalyst surface during pulsing of pent-1-ene. This was presumably as a result of hydrogenation *via* hydrogen lost from the pent-1-ene during adsorption. The majority of the species active at 110 °C were removed from the catalyst after hydrogenation. A large proportion (1.1×10^{-15} mol) of the ^{11}C adsorbed on the surface was found to be less reactive and could only be removed from the catalyst with hydrogen around 200 °C. This constituted 63.1% of the total ^{11}C species which were removed from the catalyst surface. These species have previously been described as β-carbon which has been shown to be formed from the more reactive α-carbon after prolonged periods at high temperature.[8] The total quantity of ^{11}C removed from the surface during pent-1-ene adsorption, hydrogenation at 110 °C and hydrogenation at 200 °C was 1.8×10^{-15} mol. This is somewhat less than the quantity of ^{11}C which was passed over the catalyst (7.0×10^{-14} mol). However it was observed that ^{11}C was lost from the catalyst in the form of $^{11}CO_2$ during the CO adsorption period, and during the cooling period.

The ^{11}C product selectivities from the hydrogenation reaction are shown in Fig. 1. Selectivities shown for labelled butane, pentane and hexane are the sum of both the *n*- and *iso*-components of each hydrocarbon. Of the labelled hydrocarbons higher than propane, *n*-hexane was found to be the most abundant component; in total 4.7×10^{-18} mol was isolated. This constituted 7.4% of the total labelled-hydrocarbon yield isolated during the GC injection, somewhat less than the figure of 10% observed by Koerts *et al.* for the production of propane *via* the incorporation of C_1 from methane into ethylene.[1] The percentage conversions of pent-

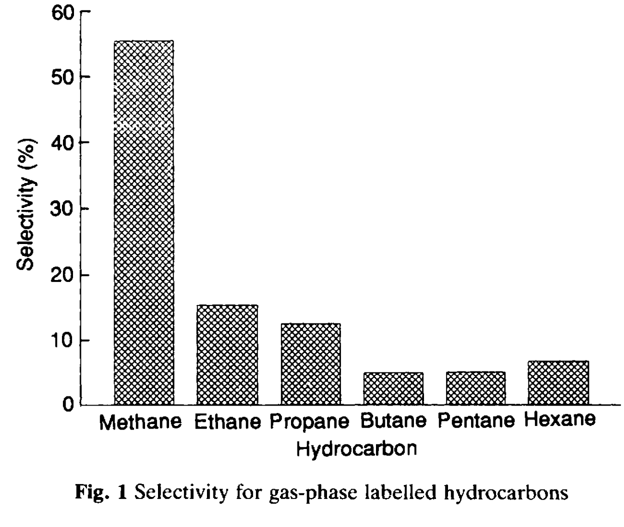

Fig. 1 Selectivity for gas-phase labelled hydrocarbons

1-ene to labelled *n*-hexane and surface ^{11}C to *n*-hexane were 1.0×10^{-10} and 0.26% respectively; these were calculated based on the quantity of *n*-hexane isolated in the GC injection. At 110 °C it was found that on the addition of hydrogen a substantial proportion of the adsorbed pent-1-ene was hydrogenolysed to shorter hydrocarbons. The reactivity of these pentene fragments with $^{11}C_1$ species is apparent from the production of ^{11}C-labelled compounds with chain lengths shorter than six carbon atoms. This is understandable as it has been shown previously that over Ru/SiO$_2$ a C_n olefin could undergo cleavage of mainly a terminal C–C bond to give C_{n-1} and C_1 fragments. The C_1 could either lead to the formation of methane, or recombine with the C_n olefin to give C_{n+1} olefins.[9]

Fig. 2 illustrates the difference in the ratios of *n*- to *iso*-hydrocarbons for both the non-labelled and labelled hydrocarbon production. The ratios of *n*-butane to *iso*-butane are not shown in the figure; however small quantities of non-labelled *iso*-butane were formed, but there was no evidence for the formation of any labelled *iso*-butane. It is clear that in the case of both pentane and hexane there is a difference between the *n*/*iso*-ratio for the labelled and non-labelled fraction; these differences were greater than those which could be attributed to experimental error. The *n*/*iso*-ratios shown in Fig. 2 were the following: pentane (non-labelled) 17.74 ± 0.89; pentane (labelled) 8.5 ± 1.4; hexane (non-labelled) 2.04 ± 0.04; hexane (labelled) 3.9 ± 0.4. The difference in the *n*/*iso*-ratio follows from the different reaction pathways leading to each product. Non-labelled hexane can be formed from the recombination of pentene fragments or from the addition of a C_1 to a surface C_5 species. The formation of labelled hexane can only come from addition of an $^{11}C_1$ species to a C_5; recombination of cracked fragments to form labelled hexane is less likely as this would involve two consecutive C–C coupling reactions. The higher *n*/*iso*-ratio for labelled hexane indicates that C_1 preferentially adds to a terminal carbon atom of the alkane chain. This is in agreement with work carried out by O'Donohoe *et al.*,[10] and with radiotracer studies carried out by Paál *et al.*,[11] which concluded that homologation occurs by the addition of C_1 units to the end carbon of dehydrogenated surface species. For non-labelled hexane production, the yield of the *iso*-fraction is therefore dominated by the recombination of cracked-pentene fragments. The far higher *n*/*iso*-non-labelled pentane ratio comes as a result of simple hydrogenation of the adsorbed pent-1-ene, which is found to be the most abundant surface species. Labelled pentane will mainly be formed from combination of a $^{11}C_1$ surface species with a C_4 fragment; however the high *n*/*iso*-ratio for labelled pentane also indicates that the C_1 is added preferentially to the terminal carbon of the alkane chain.

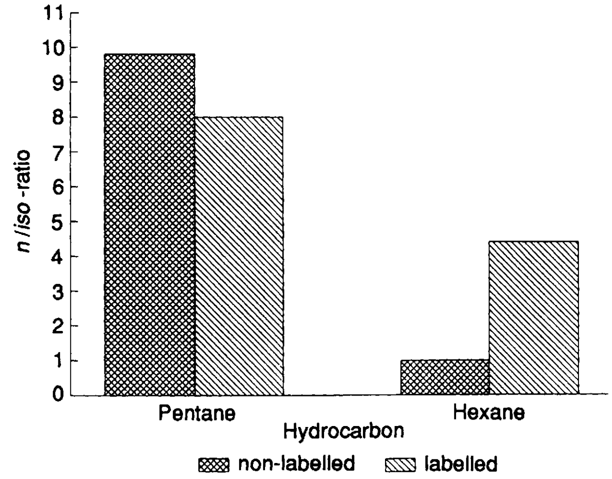

Fig. 2 *n*/*iso*-ratio for labelled and non-labelled products hydrogenated at 110 °C

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References

1 T. Koerts, P. A. Leclercq and R. A. van Santen, *J. Am. Chem. Soc.*, 1992, **114**, 7272.
2 T. Koerts, W. J. J. Welters and R. A. van Santen, *J. Catal.*, 1992, **134**, 1.
3 T. Koerts and R. A. van Santen, *J. Chem. Soc., Chem. Commun.*, 1991, 1281.
4 A. T. Bell, *Catal. Rev. Sci. Eng.*, 1981, **23**, 203.
5 M. Lecante, A. Theolier, R. Rojas and J. M. Basset, *J. Am. Chem. Soc.*, 1984, **106**, 114.
6 M. Belgued, H. Amariglio, P. Pareja, A. Amariglio and J. Saint-Just, *Catal. Today*, 1992, **13**, 437.
7 V. Matolín, M. H. Elyakhloufi, K. Masek and E. Gillet, *Catal. Lett.*, 1993, **21**, 175.
8 P. Winslow and A. T. Bell, *J. Catal.*, 1984, **86**, 158.
9 E. Rodriguez, M. Leconte and J. M. Basset, *J. Catal.*, 1991, **132**, 472.
10 C. O'Donohoe, J. K. A. Clarke and J. J. Rooney, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 345.
11 Z. Paál, M. Dobrovolszky and P. Tétényi, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 3037.