

Production of ^{11}C -labelled n-hexane for use in positron emission imaging

R.H. Cunningham, A.V.G. Mangnus, J. van Grondelle, R.A. van Santen *

Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, Netherlands

Abstract

Supported ruthenium catalysts have been used for the production of ^{11}C -labelled n-hexane via a surface reaction carried out at two different temperatures. The process involves high temperature adsorption of ^{11}CO , resulting in the production of reactive ^{11}C , surface species; this is followed by rapid cooling to a much lower temperature at which 1-pentene is adsorbed. The resultant surface species are then hydrogenated at the same temperature producing ^{11}C -labelled hydrocarbons, including n-hexane, which are concentrated and separated by on-line gas chromatography. By injecting the ^{11}C -labelled n-hexane into a catalytic reactor working under steady state conditions it is possible to use positron emission imaging to study reactions inside a working reactor.

Keywords: Isotope production; ^{11}C -labelled hexane; Hexane; Positron emission imaging

1. Introduction

Positron emission tomography (PET) is a technique which is used in the field of nuclear medicine and for other industrial applications [1–4]. The principle works by monitoring γ -photons produced as a result of the decay process of a positron emitting isotope [5]. The decay process results in the production of two photons, each travelling at 180° to each other. Detection of these photons allows one to pinpoint the position of the isotope. In medicine for example the position of labelled substances can be pinpointed inside the human body. It is clear that this technique also has industrial applica-

tions, as the energy of the photons is high enough to pass through most materials. In the field of catalysis therefore positron emission tomography would allow one to study labelled reactants inside a working catalyst bed; with conventional techniques of analysis it is only possible to study those reactants entering the catalytic reactor, and the products leaving. The technique was used fairly recently to study CO oxidation over automotive catalysts [5,6].

A few years ago a project was initiated to build a system for positron emission studies in Eindhoven making use of the University's cyclotron. In principle it would be possible to study a number of catalytic reactions using this facility, however, our main interest lay primarily with studying the hydroisomerization of n-hexane over zeolite catalysts. In our study we

* Corresponding author.

wished to study the reaction under steady state conditions. One major advantage of positron emitters is their high specific activity, which means that only very small quantities of labelled material are required to produce significant results. Small quantities of labelled material could therefore be injected into a reactant stream entering a reactor without running the risk of disrupting the steady state conditions.

When designing the detector system, the flow of gases through the catalytic reactor was assumed to be a one dimensional problem, i.e. only changes in the molecular concentrations along the length of the reactor would be studied, and any changes which may occur in a radial direction inside the reactor were ignored. This assumption significantly simplified the design for the detector system; a detector system consisting of only two banks of detectors was finally designed and constructed [7], instead of the standard multi-detector bank PET detector. As the detector would only be able to pinpoint labelled molecules as a function of distance along the catalyst bed, we have called the detection technique positron emission profiling (PEP) rather than positron emission tomography (PET).

In order to label the n-hexane with a positron emitting isotope, the technique developed earlier in this laboratory for the homologation of alkenes was used [8]. In that study it was shown that carbon atoms from $^{13}\text{CH}_4$ could be inserted into ethylene or propylene to produce labelled propane or butane respectively. In this recent study ^{11}C is used as the source of C_1 .

2. Experimental

2.1. ^{11}C production

^{11}C , a positron emitting isotope, has a half life of 20.39 min and is produced via reaction (1): bombardment of high purity nitrogen with 12 MeV protons, accelerated in the cyclotron. A typical 25-min irradiation period of 3.5 l of gas results in the production of 300 MBq of activ-

ity; this is equivalent to approximately 1 pmol of ^{11}C .



Small oxygen impurities inside the target vessel, and the high energy involved are sufficient to convert all ^{11}C produced to $^{11}\text{CO}_2$. $^{11}\text{CO}_2$ produced in the nitrogen target vessel is first concentrated in a liquid-nitrogen cooled spiral before being passed through a zinc reactor operating at 380°C. In this way the $^{11}\text{CO}_2$ is converted with 100% selectivity to ^{11}CO .

Positrons emitted from the ^{11}C nucleus travel only a relatively short distance (1.6 mm in catalyst matter) before being annihilated with an electron. However, the resultant 511 keV γ -photons are able to travel a much greater distance, and it is possible to detect these outside the reactor walls.

2.2. ^{11}C -labelled n-hexane production

For the homologation reaction, Ru/SiO₂ catalysts have been used, and promotion of these catalysts with vanadium has been found to greatly increase the yield of higher hydrocarbons. The catalysts were all produced via incipient wetness impregnation of Grace silica (surface area 240 m² g⁻¹ and pore volume 1.65 ml g⁻¹) with acidic aqueous solutions of RuCl₃ and NH₄VO₃. All catalysts were dried and reduced in flowing hydrogen at 400°C for 4 h before use. The performance of four catalysts will be discussed in this paper: 5%Ru/SiO₂, 5%Ru–0.33%V/SiO₂, 5.3%Ru–0.7%V/SiO₂ and 5.3%Ru–1.4%V/SiO₂.

The apparatus used for labelling experiments is similar to that described in previous papers [9,10], however, some modifications have been made to improve the yield of n-hexane. The apparatus consists of a quartz micro reactor, approximately 6 ml in volume, and containing approximately 400 mg of catalyst. Labelled hydrocarbons are produced by adsorption and dis-

sociation of ^{11}CO on the metal catalyst at a temperature between 300 and 350°C. Following this the catalyst is cooled rapidly to a temperature of 110°C at which 1-pentene is adsorbed. The resultant surface species are then hydrogenated to form products at the same temperature used for 1-pentene adsorption. During experiments helium is continually passed over the catalyst; the introduction of helium and hydrogen to the reactor are controlled by 24-volt solenoid valves, and the gas flow-rates are controlled by Brooks 5850 TR thermal mass-flow controllers. Non-labelled carbon monoxide and 1-pentene are introduced to the reactor via electrically operated six-way valves (Valco). ^{11}C -labelled carbon monoxide is introduced to the system via a simple three-way valve. All gases leaving the reactor can be passed through a stainless steel liquid-nitrogen cooled spiral, in which the higher hydrocarbons formed are condensed. Rapid heating of the cooling spiral by using a small electrical potential allows the hydrocarbons to be injected into the on-line GC

in the form of a concentrated pulse. The GC is a Packard model 427 fitted with a TCD and 2-m squalane/chromosorb column. The GC is able to completely separate all C_{3+} products at a temperature of 80°C. Following separation n-hexane is condensed and concentrated in a second cooling spiral; rapid heating of the concentrated n-hexane allows injection in the form of a narrow pulse into the hydrogen/n-hexane reactant stream entering the hydroisomerization reactor and PEP detector system. Four NaI scintillation detectors are positioned in the apparatus to monitor the radioactivity at various stages of the reaction: detector 1 measures the total activity entering the laboratory, and hence passing through the reactor; detector 2 measures the activity after product separation in the GC; detectors 3 and 4 measure respectively the activity before and after the first liquid-nitrogen cooled spiral, and so give an indication of the efficiency of the concentration process. The apparatus used for labelled alkane production is illustrated in Fig. 1.

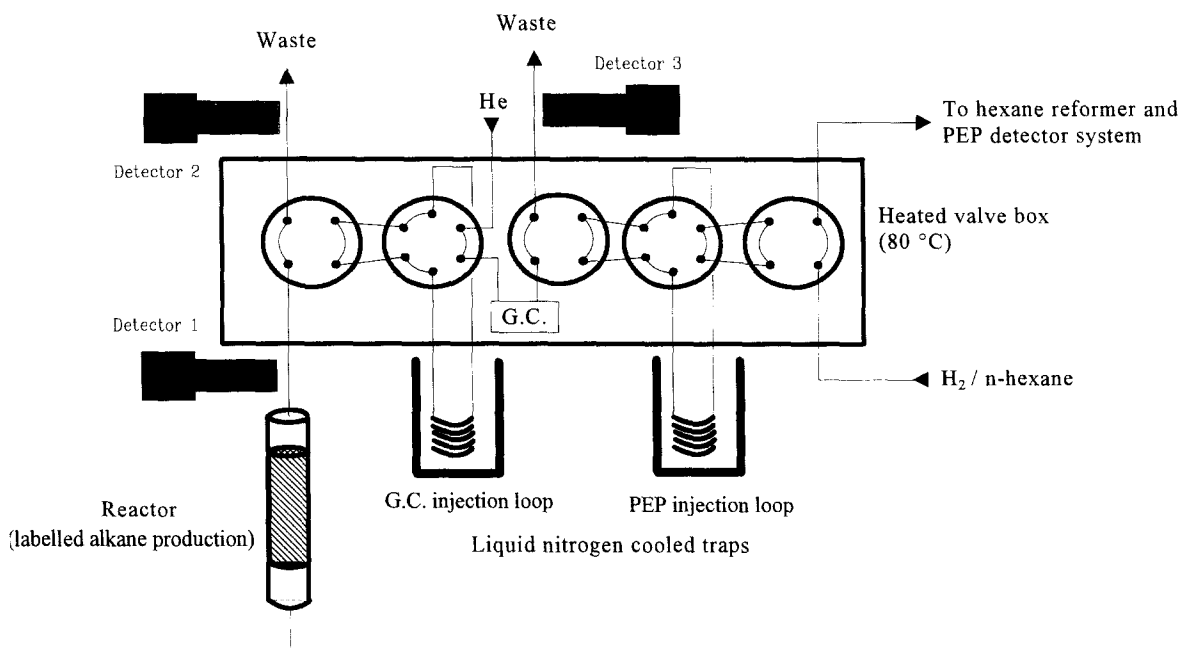


Fig. 1. Apparatus for collection, concentration and injection of labelled n-hexane

3. Results and discussion

3.1. High temperature $^{11}\text{C}_1$ formation

During the high temperature adsorption it is generally accepted that three types of surface carbon species are formed, and these are generally referred to as C_α , C_β and C_γ [11–13]. TPR studies of the ^{11}C surface species has shown evidence for the existence of both C_α and C_β with maxima in $^{11}\text{CH}_4$ production at 110°C and 200°C, respectively. In no experiments, however, was there any evidence for the formation of C_γ on any of our catalyst samples.

The formation of C_1 surface species from CO at high temperature is generally believed to take place via the Boudouard reaction [11,14]. This is confirmed from our experiments where the production of $^{11}\text{CO}_2$ has been observed during high temperature adsorption of ^{11}CO . In order for ^{11}C to remain adsorbed on the metal surface, the co-adsorption of non-labelled CO has been found to be an essential step with the pure Ru/SiO₂ catalyst, but, this step is not so important for the vanadium promoted catalysts. Studies on supported Rh catalysts [15] have suggested that CO can perform a cleaning role, removing traces of surface oxygen; we believe that non-labelled CO is performing the same role with our pure Ru catalyst. We have also found that it is important that the non-labelled CO is passed over the catalyst prior to the introduction of ^{11}CO rather than simultaneously, as simultaneous adsorption of ^{11}CO and non-

labelled CO also leads to substantial loss of ^{11}C from the catalyst. This result suggests further that the non-labelled CO is performing primarily a cleaning role.

3.2. Effect of vanadium promotion on labelled n-hexane selectivity

In principle starting from adsorbed C_1 and 1-pentene one would expect that methane and n-hexane would be the only labelled hydrocarbons formed. However, a range of labelled hydrocarbons is produced from methane through to hexane, including iso-alkanes. This comes 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 can react equally well with the shorter carbon fragments formed from 1-pentene as with non-dissociated adsorbed 1-pentene, and a similar result has also been observed by other authors studying the self homologation of alkenes [16].

The effect of vanadium promotion on n-hexane selectivity and type of surface carbon formed has been investigated and the results are summarised in Table 1. It can be seen that promotion of the Ru catalyst with vanadium increased the fraction of carbon which was adsorbed in the reactive C_α form. The selectivities for products produced from this C_α fraction are also found to be affected by vanadium promotion: the n-hexane selectivity is seen to pass through a maximum with 0.33 wt.% V. In agreement with previous studies [13], we have

Table 1
Product selectivities and selectivity towards C_α formation for various Ru/SiO₂ catalysts

Catalyst	Product selectivity, %						C_α fraction	Total n-hexane selectivity, %
	Methane–propane	Butane	i-Pentane	n-Pentane	i-Hexane	n-Hexane		
5%Ru/SiO ₂	69.0	3.2	0.8	7.3	3.1	16.6	0.091	1.51
5%Ru–0.33%V/SiO ₂	66.6	3.3	0.7	4.8	4.6	20.1	0.210	4.23
5.3%Ru–0.7%V/SiO ₂	76.1	3.6	0.3	4.7	2.1	13.2	0.161	2.13
5.3%Ru–1.4%V/SiO ₂	82.6	4.2	0.7	3.5	2.7	6.3	0.234	1.47

All product selectivities were measured during hydrogenation at 110°C.

found that C_{2+} hydrocarbons are only formed from the C_{α} surface species. From this a total selectivity towards n-hexane can be calculated based on the total quantity of ^{11}C adsorbed. This also shows a maximum value with 0.33 wt.% V. Promotion of the catalyst with a small quantity of vanadium therefore increases the chance of reactive C_{α} formation, and increases the likelihood that this reactive carbon will form n-hexane.

Vanadium promotion is believed to increase n-hexane production in two ways. Firstly, by reducing the size of the Ru ensembles, so reducing the catalyst's hydrogenolysis activity; we have already seen evidence for the beneficial effect of blocking Ru sites [9], where the introduction of a large quantity of non-labelled CO to the reactor during the high temperature adsorption period was found to dramatically increase the selectivity towards n-hexane production. Secondly vanadium is thought to act by increasing the metal-carbon bond strength, making C-C coupling reactions more likely than hydrogenation of small carbon fragments to form short-chain hydrocarbons. This conclusion was also reached in previous studies carried out over Rh catalysts [17].

3.3. Injection of ^{11}C -labelled n-hexane into a non-labelled gas stream

The technique used for the concentration of the product hydrocarbons prior to GC injection has proved to be extremely effective. By concentrating the product hydrocarbons using low temperatures the quantity of labelled material which can be injected into the GC is approximately five times greater than that which could be injected using our previous on-line analysis system. The effectiveness of the liquid-nitrogen cooled traps is illustrated in Fig. 2 where the signal for the NaI detector placed at the outlet of the GC (detector 2) is plotted. Trace A in Fig. 2 shows the retention times and signals for 2-methylpentane, 3-methylpentane and n-hexane following separation in the GC. Trace B illus-

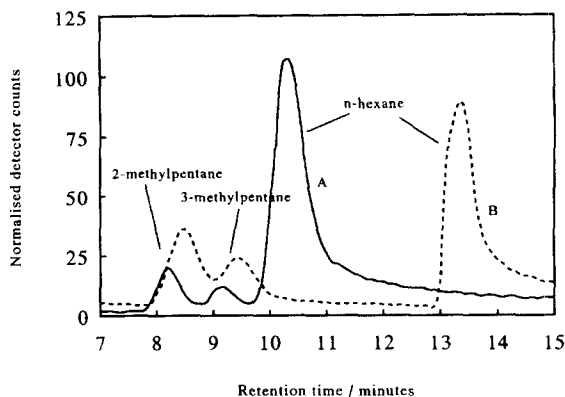


Fig. 2. GC plot showing effectiveness of cooling/flash-heating technique. Trace A: standard retention times for 2-methylpentane, 3-methylpentane and n-hexane. Trace B: retention times following separation of n-hexane in the liquid-nitrogen cooled trap.

trates the use of the second liquid-nitrogen cooled trap following hydrocarbon separation. The diversion of the n-hexane flow through the trap (Fig. 1) resulted in all of the labelled product being trapped, this can be seen as the n-hexane signal is no longer present at the normal retention time of 9.8 min. Following a period of 3 min the second cooling spiral was heated and this resulted in the immediate detection of the labelled n-hexane peak by the NaI detector. It was found that the trapped n-hexane could also be easily injected into a separate non-labelled gas stream which was flowing through the PEP detector system.

4. Conclusions

Promotion of the Ru catalyst with V has been found to greatly increase the catalyst's selectivity towards n-hexane production. This comes about partly through an increase in the metal-carbon bond strength in the case of the promoted catalyst. The improved method of product concentration and separation has also greatly increased the yield of labelled n-hexane. It appears that a sufficient quantity of ^{11}C -labelled n-hexane can be produced and isolated to be used in the study of the hydroisomerization of n-hexane.

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