Imaging of hydrocarbon reactions in zeolite packed-bed reactors using positron emission profiling

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Received 20 July 1998; accepted 13 October 1998

The ability of positron emission profiling (PEP) to measure concentration profiles of molecules labelled with positron-emitting nuclei, such as ^{11}C, ^{13}N, and ^{15}O, inside chemical reactors has been demonstrated for the system n-hexane–Pt/H-zeolites under conditions typical of the hydroisomerization reaction. Data obtained in the absence of reaction were first measured and used to model mass transport processes in these biporous, packed-bed reactors. Images obtained under conditions where injected, labelled pulses underwent reaction revealed that the products did not exit the reactor and thus demonstrated the need for *in situ* measurement. Such experiments should provide a valuable new tool in the study of transient, initial phenomena so often of importance in heterogeneous catalysis, such as “preconditioning” and deactivation.

Keywords: positron emission profiling (PEP), *in situ* study, transient kinetics, hexane hydroisomerization, acidic zeolite catalysts

1. Introduction

Chemists and chemical engineers studying the kinetics of heterogeneously-catalysed reactions are constantly trying to answer questions regarding the chemical nature of reacting species and the rates with which these species undergo transformations. Many spectroscopic and surface science techniques have been successfully applied to this problem over the past thirty years and have generated a large body of data. As these data have generally been obtained under conditions differing from the actual process a link must be made back to the original systems of interest occurring in chemical reactors at elevated temperatures and at atmospheric pressure and above. Mathematical models based on previously determined mechanistic information provide this link.

Mathematical models of reactor kinetics attempt to describe the concentration distributions of various reactants, intermediates and products within the reactor during the course of the reaction. In order to validate these models concentration distributions must be measured. However, as these chemical reactions generally occur within metal reactors enclosed by a heating mantle it is not a simple matter to “look inside”. Rather most techniques rely on a “what went in and what came out approach”. That is to say that measurements of concentration distributions are measured at the reactor inlet and outlet only.

In order to measure concentration profiles within an operating reactor it is necessary to employ probes that are capable of penetrating the reactor and the oven. As gamma photons possessing energies in excess of several hundred kiloelectron volts (keV) are able to penetrate a few centimeters of stainless steel they are suitable probes. As described in the paper by Jonkers [1], positron emission imaging, which is based on the coincident detection of two gamma photons arising from a single positron-electron annihilation event, was first applied to make such concentration measurements in reactors some five years ago [2,3]. These studies used a so-called positron emission tomograph (PET) camera that was designed to generate three-dimensional images of concentration profiles of positron-emitting radiotracers within organs of a living human. Although the detector used was not optimised for the task, Vonkeman et al. demonstrated the potential of the technique by measuring one-dimensional concentration profiles (along the cylindrical axis) of injected positron-emitting radiotracers such as: ^{11}CO, ^{11}CO$_2$, C^{15}O, ^{15}OO within a packed-bed reactor containing a cerium-promoted Pt/γ-alumina catalyst under steady-state conditions [2,3]. The measured concentration profiles were then used to refine a model of the kinetics of reactions occurring on this simulated three-way exhaust catalyst.

Since the early 1990’s a facility has been developed at the Eindhoven University of Technology dedicated to the application of positron emission imaging to catalysis research. The project is a collaborative effort between the

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Faculties of Chemical Engineering and Technical Physics. This paper will describe the facilities presently available and will discuss recent research involving the application of positron emission imaging to study physical and chemical phenomena related to the hydroisomerization of n-hexane on Pt/acidic zeolites under typical process conditions.

2. The positron emission profiling (PEP) detector

As stated above, Vonkeman et al. used a commercial PET camera for their experiments. This camera was designed to obtain data in three dimensions, a process which requires in excess of 15 min to acquire sufficient data. As the retention time of a radio-labelled pulse in the single-pass flow reactor was typically of the order of tens to hundreds of seconds there was insufficient time to acquire three-dimensional images. Only one-dimensional images, along the cylindrical axis could be obtained. Fortunately, under axially-dispersed plug flow conditions, concentration gradients in the radial direction are negligible. Hence, the concentration profiles, consisting of measurements every 11 mm at 1.2 s intervals were sufficient.

Obviously, if concentration profiles in a single dimension are sufficient one does not have to use a costly 3D scanner to measure this data. A positron emission detector has, therefore, been developed that is specifically tailored to the measurement of activity distributions as a function of time along a single, axial direction, i.e., specifically tailored for studies in tubular reactors [4]. The detector has been named a positron emission profiling (PEP) detector. The term “profiling” underlines the difference with respect to a three-dimensional tomographic, PET scanner. The estimated cost of development and production of the PEP detector is ca. \$ 300,000 (US) or less than $1/10$th the current cost of a commercial PET camera.

The positron emission profiling (PEP) detector is shown in figure 1. It has been designed to be flexible so that

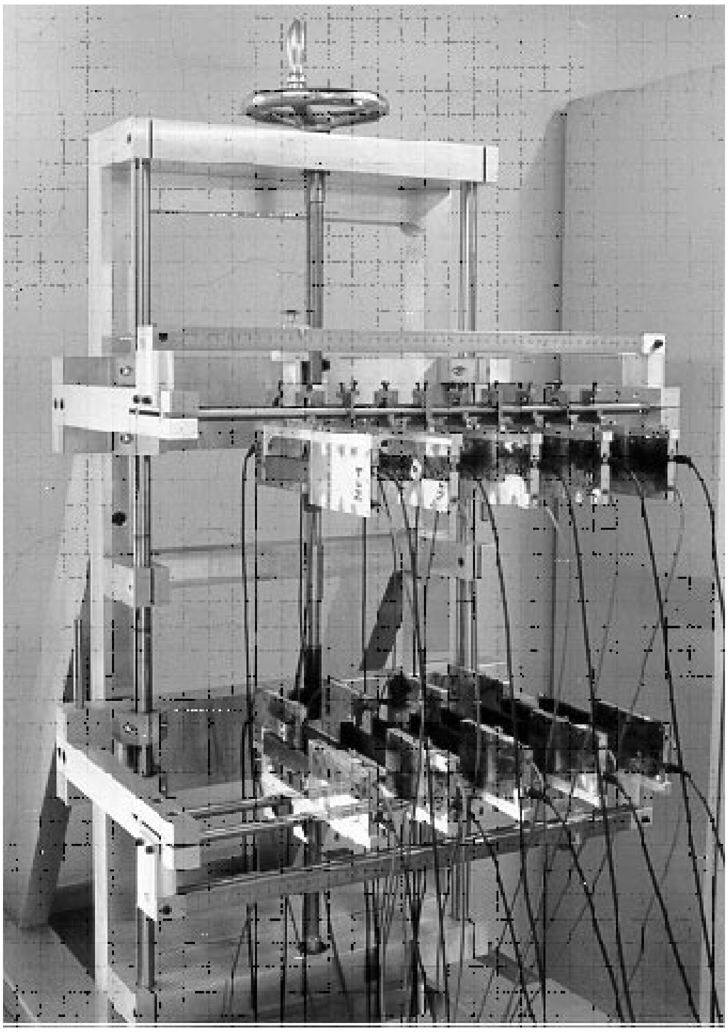


Figure 1. A photo of the positron emission profiling (PEP) detector. The detector consists of two horizontally-mounted arrays each containing nine independent detection elements. Each detection element consists of a bismuth germanium oxide (BGO) scintillation crystal coupled with a photomultiplier. The eighteen detection elements are situated in a frame that allows adjustment in order to accommodate reactors of bed lengths between 4 and 50 cm and diameters of up to 25 cm.

it could be used with a variety of different sizes of reactors; measurements can be carried out on reactors having bed lengths between 4.0 and 50 cm and diameters of up to 25 cm. The detector consists of two arrays of nine independent detection elements each and is mounted horizontally with the reactor and furnace placed between the upper and lower arrays. Each detection element consists of a bismuth germanium oxide (BGO) scintillation crystal coupled to a photomultiplier. The eighteen detection elements are situated in a frame that allows adjustment of the overall detector dimensions if required.

The detection principle is as follows. Each detector element in a bank can form a detection pair with each of the elements in the opposite bank; the two banks of nine elements, therefore, form 81 (9^2) possible detection pairs. Coincident detection of the two 511 keV gamma photons, formed during positron–electron annihilation, is used to locate the position of the event along the cylindrical axis of the bed at the point at which the chord joining the two elements intersects this axis. Due to redundancy, the set of chords joining these 81 detection pairs results in 17 ($(2 \times 9) - 1$) unique, equidistant positions along the cylindrical axis.

Temporal information is obtained by collecting data during a fixed sampling period. A minimum integration time of 0.5 s is required to obtain sufficient coincident events for reliable statistics and for on-line computation; thus the temporal resolution is 0.5 s.

When the detector block is in its “close-packed configuration”, i.e., when all of the detector elements are placed tightly together, the spatial resolution of the detector is 2.9 mm. This is comparable to state of the art 3D PET detectors and is near the theoretical limit of the spatial resolution governed by the range of the positrons under study (the stopping distance).

In order to reduce errors resulting from the detection of Compton scattered photons which lead to anomalous positioning of annihilation events, energy selection of the photons is also employed. Coincident events which have a measured energy below the lower limit of a window centered at 511 keV are rejected as being due to scattered photons. Since the energy resolution of BGO scintillators is poor this window is quite large (350–700 keV).

In summary, the above detection principle can be employed to obtain profiles of the average concentration of all radio-labelled components contained within volume segments (of lengths greater than or equal to 3 mm) within the imaged specimen at time intervals of 0.5 s.

3. Synthesis of $^{11}CH_3C_5H_{11}$

Before PEP could be applied to study reactions of n-hexane on zeolites a method to synthesise carbon-11 labelled n-hexane was necessary [5]. As the half-life of carbon-11 is only 20 min it must be prepared on-site, typically via nuclear reaction induced via an energetic beam of protons as supplied by a cyclotron or other particle accelerator. For example, carbon-11 can be synthesized by irradiating a target of gaseous nitrogen-14 with 12 MeV protons during which time the following nuclear reaction occurs:

$$^{14}\mathrm{N} + \mathrm{p} \rightarrow {}^{11}\mathrm{C} + \alpha$$

Oxygen impurities in the target gas are sufficient to oxidise all of the carbon-11 produced to $^{11}CO_2$.

The labelled carbon dioxide produced (ca. 10^{-12} moles produced during a 20 min irradiation period) is then reduced to ^{11}CO over zinc. Labelled CO is then used in a two-step alkene homologation reaction previously developed in this laboratory [6]. ^{11}CO is pulsed over a vanadium-promoted Ru/SiO_2 catalyst at 350 °C. The temperature is then rapidly reduced to between 90 and 120 °C and 1-pentene is pulsed over the catalyst. Desorptive hydrogenation is then performed. As homologation of shorter alkanes, resulting from cracking of 1-pentene on Ru, also occurs, a range of alkanes is produced from C_1 to C_6. The hydrocarbons are separated by a process of freezing, flash-heating and gas chromatography. The desired product (approximately 1–3 Mbq or 10^{-15} mole of $^{11}CH_3C_5H_{11}$) is then frozen out ready for injection. If so desired, one of the other labelled alkane fractions can be isolated and injected. The radio-labelled fraction is minute compared with the amount of non-labelled n-hexane that is produced as the total amount of the injected pulse is typically on the order of 10^{-6} moles. The production process (i.e., the adsorption of ^{11}CO on Ru/SiO_2 and the GC separation) can be monitored by NaI scintillation detectors. The process has been optimized such that pulses of radio-labelled n-hexane can be prepared every 45 min, if desired.

4. The hexane reformer system

Reactions of hexane were studied in packed-bed reactors of Pt/H-zeolites. Figure 2 shows a schematic diagram of the single-pass flow reactor system. As shown, the reactor and water-jacketed oven are placed in between the banks of the detector. Reactions performed under steady-state conditions using mixtures of non-labelled n-hexane in hydrogen could be followed using an on-line gas chromatograph equipped with an FID detector. Pulses of labelled n-hexane were made into the inlet feed stream of the reactor under steady-state conditions or under transient conditions. The radio-labelled pulse could be measured within the reactor bed using the PEP detector. Radio-labelled products could also be trapped after the reactor using a liquid-nitrogen-cooled spiral. Trapped products were subsequently analysed via GC using a sodium iodide scintillator detector. It is important to stress at this point that the flow system, reactor bed, temperatures employed, etc. differed in no way from those normally used in the laboratory. Therefore, measurements are truly made under typical reaction conditions.

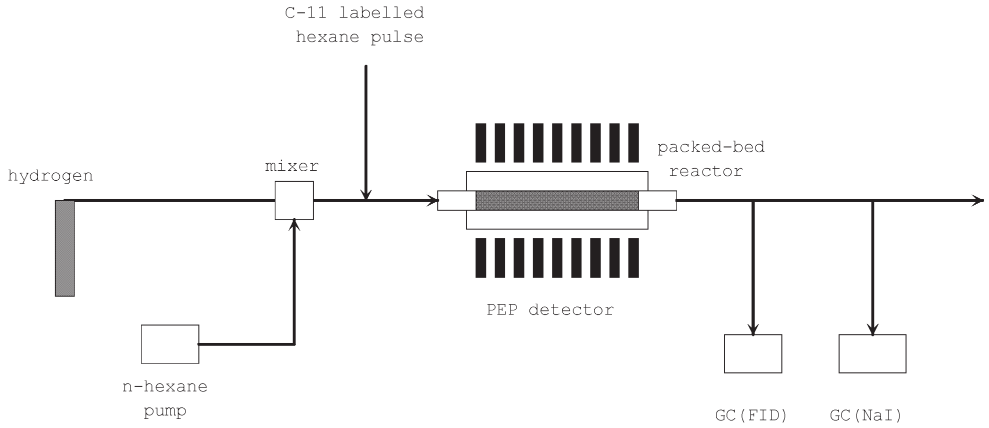


Figure 2. A schematic diagram of the single-pass flow reactor system. As shown, the reactor and water-jacketed oven are placed in between the banks of the detector. Reactions performed under steady-state conditions using mixtures of non-labelled n-hexane in hydrogen could be followed using an on-line gas chromatograph equipped with an FID detector. Pulses of labelled n-hexane were made into the inlet feed stream of the reactor under steady-state conditions or under transient conditions. Radio-labelled products could also be trapped after the reactor using a liquid-nitrogen-cooled spiral. Trapped products were subsequently analysed via GC using a sodium iodide scintillation detector.

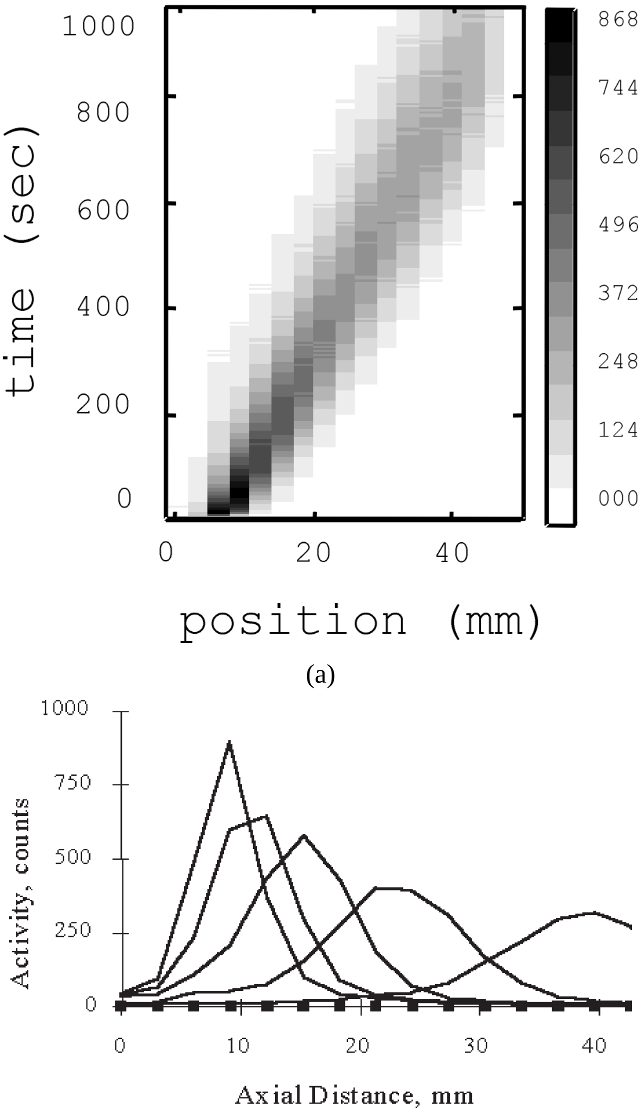
5. Measurement of adsorption and diffusion of hexane on H-zeolites

The hydroisomerization of n-hexane on Pt/H-zeolites is known to proceed via a bifunctional mechanism in which hexane is first dehydrogenated on platinum followed by isomerization of the resultant alkene on a Brønsted acid site and is finally rehydrogenated to the final alkane on platinum [7]. No isomerization of hexane occurs on the acidic zeolite in the absence of platinum at temperatures below ca. 400 °C due to the much larger activation energy of formation of carbonium ions compared to that of carbenium ions. This allows adsorption and mass transfer of hexane to be studied independently from reaction on acidic zeolites in the absence of platinum over the same temperature region (to ca. 260 °C). Thus mass transport, which often plays an important role in transient kinetic experiments, can be modelled separately and the results can be used later in models including reaction.

The application of PEP to the measurement of hydrocarbon adsorption and diffusion in zeolites is simply a modification of the so-called “pulse gas chromatographic technique” which was developed in the late 1950’s and the early 1960’s and is an extension to the “tracer pulse GC method”. All of these techniques are based on measurement of the retention time of an injected pulse of an adsorbable gas within a column packed with the adsorbent of interest. In the tracer pulse GC method carbon-14 is used to label the hydrocarbon molecules instead of carbon-11. Carbon-14 decays by β^--emission and the electrons released cannot penetrate the stainless reactor. Measurements of the pulse are made using ionization detectors placed at the inlet and outlet of the reactor bed. If the pulse passes through the reactor in a fairly predictable manner, as is the case if only adsorption and dispersion processes occur, then the resulting data are quite sufficient, as demonstrated by the work of Danner et al. [8]. It will become more apparent later when dealing with reacting pulses that *in situ* measurement of these profiles is very necessary.

Figure 3(a) shows a typical PEP image obtained following the injection of an $^{11}CH_3C_5H_{11}$ pulse into a hydrogen feed stream (150 ml/min) flowing through a packed-bed reactor containing the zeolite H-mordenite at 150 °C. Circa 200 mg of pelletized zeolite (250–500 μm) was typically used to form a packed column 42 mm in length and 4 mm in diameter. The figure is a two-dimensional representation of the measured activity–time–position surface. The total measured activity (and, hence, concentration) is plotted at various positions and time intervals within the reactor. The measured concentration is indicated by the grey-scale with increasing intensity indicating increasing activity. As shown in the figure, the pulse progressed linearly through the bed with respect to time. The total retention time was 941 s. The retention time of the pulse is dependent on the adsorption strength of the alkane in the zeolite. By repeating such an experiment over a range of temperatures one can measure the enthalpy of adsorption of this process.

The degree to which the labelled alkane is adsorbed by the zeolite is most critical in determining if PEP measurements can be made. As stated above, measurement times of 0.5 s are necessary in order to obtain sufficient statistics for a reliable concentration measurement. As a “meaningful” profile would preferably contain ten such concentration points, a hold-up of at least 5 s is necessary in order to obtain a useful PEP image using the existing detector. Thus, the study of hexane adsorption on a zeolite such as H-mordenite (containing no preadsorbed hexane) is limited to a maximum measurable temperature of ca. 300 °C. For zeolites that adsorb hexane to a lesser extent, e.g., H-ferrierite and H-ZSM-22, this temperature is reduced to ca. 230 °C. Of course, preadsorption of hexane will reduce the retention time still further due to the lower number of available adsorption sites. The latter is important if one wishes to measure PEP images under steady-state reaction conditions.



(a)

(b)

Figure 3. (a) A PEP image obtained when a pulse of $^{11}CH_3C_5H_{11}$ (10^{-15} moles or 1 MBq) was injected into a stream of hydrogen (150 ml/min) at 150 °C flowing through a bed of H-mordenite (250–500 μm). Only adsorption and mass transport of n-hexane occurred under these conditions. The horizontal scale gives the position along the catalyst bed. The vertical scale indicates the residence time. The grey-scale indicates the concentration of the ^{11}C-label according to the linearly-scaled colour bar. (b) Horizontal cross-sections that were taken from the data set shown in 3(a). These cross-sections represent the measured activity as a function of position at different retention times in the bed. Cross-sections measured at 25, 50, 100, 200, and 400 s are shown.

This measurement limitation due to retention time is at the same time advantageous. As gas-phase components traverse the reactor in a few hundreds of a second at these temperatures and flow rates, one can be certain that the measured PEP image is the result of labelled components in the adsorbed phase only.

If cross-sections are taken at various constant values along the y-axis of figure 3(a) one obtains curves of the measured activity as a function of axial position at constant time. Figure 3(b) shows these curves measured at 25, 50, 100, 200, and 400 s. As predicted by theory, these peaks are Gaussian in shape and decrease exponentially with respect to both time and position [9].

The broadening of the peaks is caused by dispersion due to mass transport processes. As packed-bed reactors composed of pellets of compressed zeolite crystallites form a biporous system mass transport occurs: between the pellets, across a static film surrounding the pellets, in macropores within the pellets, and in addition to the diffusion processes occurring within the micropores of the zeolite crystals.

PEP experiments were performed to measure the rates of these different processes using packed-beds made from: H-mordenite, H-beta, H-ZSM-5, H-ZSM-22, and H-ferrierite. Images were recorded following injections of labelled n-hexane into a hydrogen gas carrier at various flow rates and at temperatures between 170 and 230 °C. Experiments were also performed using different pellet or crystallite sizes. Diffusion constants for hexane in the zeolite were determined by applying the so-called “method of moments” to the measured profiles [10], or by fitting the measured activity–position–time surface to a mathematical model based on the time-dependent mass balance equations for a biporous packed-bed adsorber [11].

The results of the above analysis revealed that mass transport of hexane through beds of H-ZSM-5 pellets (250–500 μm diameter) at these temperatures was controlled by axial dispersion, film transfer and by macropore diffusion rather than by diffusion in micropores. Only in smaller pore zeolites such as H-ferrierite and H-ZSM-22, did micropore diffusion have a large contribution to overall mass transfer limitations (ca. 50%)

6. PEP measurements under reaction conditions: measurement of transient reaction phenomena using PEP

The ability of PEP to measure *in situ* concentration distributions of a labelled radio-tracer as a function of both position and time with short sampling times enables it to be used to study processes that are transient and highly spatially-dependent. Studies of the initial rate of catalyst deactivation or preconditioning are two areas where PEP seems particularly valuable. Reactions of hexane on freshly-reduced platinum particles dispersed in an acidic zeolite have been studied using PEP and the results will be described here as one example.

Pt/H-mordenite is highly selective under steady-state conditions towards isomerization although platinum metal is known to be a good catalyst for hydrogenolysis. The state of the platinum metal under these conditions is, therefore, of considerable interest. Efforts to determine such information are complicated by the fact that surface species are highly sensitive to experimental conditions but must often be determined under different conditions for experimental reasons.

Figure 4 shows a series of PEP images obtained following a pulse of labelled n-hexane into a hydrogen stream

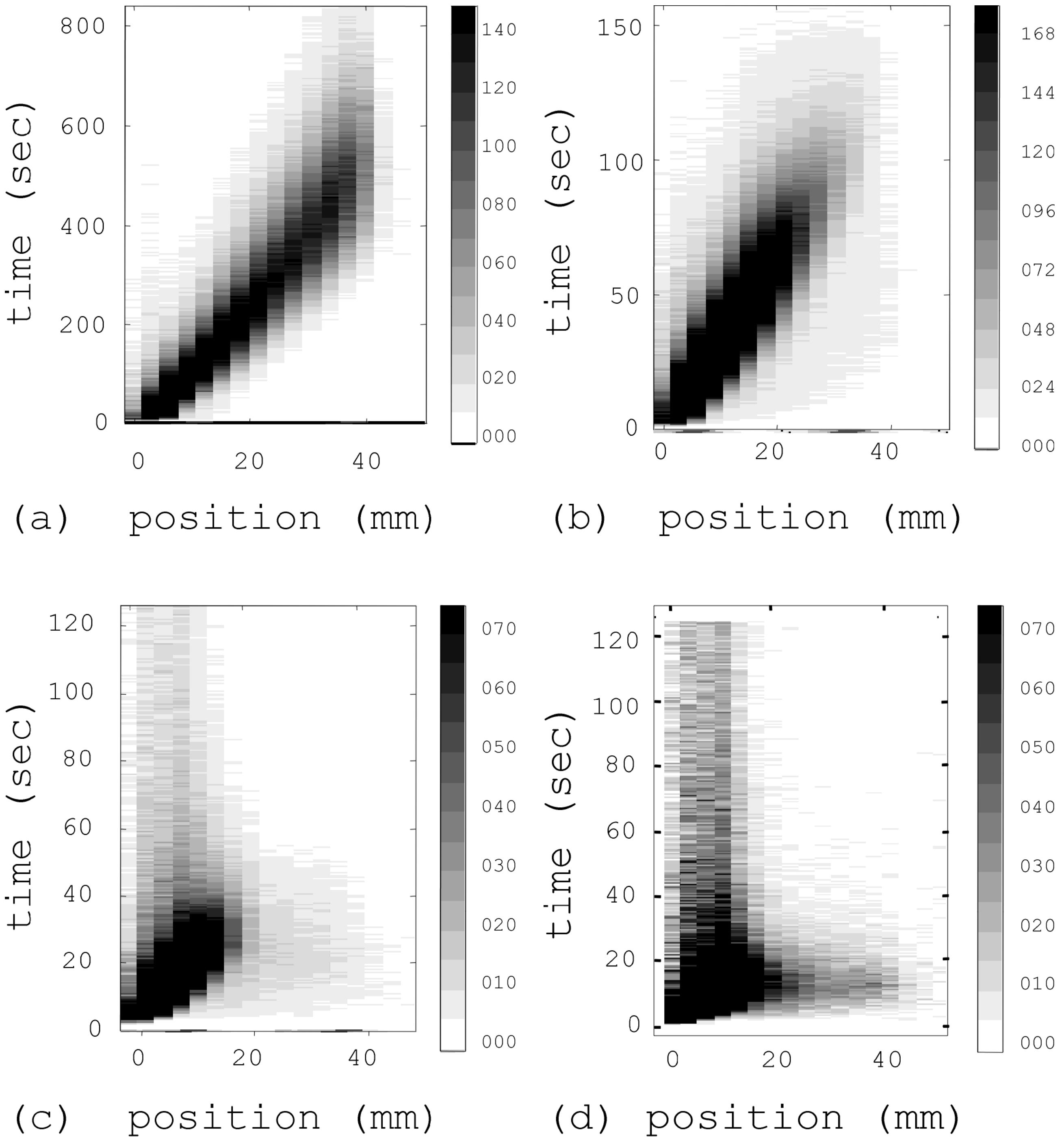


Figure 4. PEP images recorded following pulse injection of C-11 labelled n-hexane into a hydrogen feed stream (150 ml/min) flowing through a reactor containing freshly-reduced 2 wt% Pt/H-mordenite catalyst at: (a) 150 °C, (b) 190 °C, (c) 210 °C, and (d) 230 °C. At 150 °C only adsorption and diffusion of the pulse was observed. At higher temperatures hydrogenolysis of n-hexane on the fresh Pt surfaces is clearly visible at the front of the reactor bed. The light hydrocarbons products (labelled C_1 to C_3 hydrocarbons) can be seen rapidly exiting the reactor (within ca. 20 s) in (c) and (d). The carbonaceous overlayer formed on the catalyst surface appears as vertical band at beginning of the bed.

flowing through a packed bed of 2.0 wt% Pt/H-mordenite. In each case the platinum was first reduced in flowing hydrogen at 400 °C for 30 min prior to the injection at the temperature indicated. At a temperature of 150 °C, figure 4(a), the pulse appears to undergo only adsorption and diffusion (cf. figure 3(a)). Radio GC analysis of the effluent indeed revealed only n-hexane. However, as the injection temperature was increased (figure 4 (b)–(d)) the PEP images changed considerably. In figure 4 (c) and (d) it is obvious that the pulse of n-hexane began to react near the front of the reactor bed, some of the activity exited the reactor very quickly (within ca. 20 s) and some of the activity remained on the catalyst surface. Analysis of the radiolabelled reaction products by trapping and subsequent GC

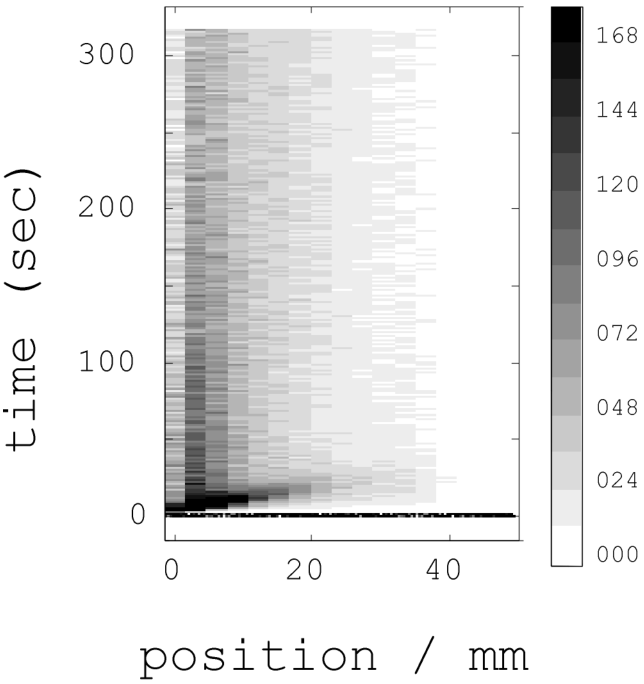


Figure 5. PEP image of a pulse of n-$^{11}CH_3C_5H_{11}$ in a 2 wt% Pt/H-mordenite catalyst that was previously used in the steady-state hydroisomerization reaction (n-hexane (10 μl/min) in hydrogen (150 ml/min)) at 240 °C. Hydrogen was then used to empty the bed of absorbed hexane (20 min). The feed stream was then switched to helium (75 ml/min) and the injection of n-$^{11}CH_3C_5H_{11}$ was made. The majority of the n-hexane was rapidly dehydrogenated to hexene by the Pt sites at the front of the bed. These hexenes were subsequently immobilized by irreversible adsorption (in the absence of hydrogen) on the Brønsted acid sites and appear as the vertical band in the spectrum. Unreacted hexane continued through the reactor as before. Small amounts of C_1, C_2, C_7, and C_8 (formed by dimerization and cracking) were also detected via radio GC analysis of the trapped effluent in addition to C_6.

separation using a NaI scintillation detector revealed light alkanes between C_1 and C_3. The remainder of the activity remained ad infinitum within the first 10 mm of the catalyst bed (appears as a vertical band). This remaining band could be completely removed by temperature-programmed hydrogenation to 400 °C. Trapping and subsequent analysis of the products revealed only methane [12].

The behaviour observed in figure 4 is due to the hydrogenolysis of n-hexane on the freshly-reduced platinum surface sites. The vertical band at the front of the bed is due to the formation of a carbonaceous overlayer on the platinum surface. This is clearly one example in which the ability to measure product concentrations inside the reactor is necessary. This example also reveals the potential of using PEP to study initial phenomena.

Quite different behaviour was observed when the Pt/H-mordenite catalyst was first used in the steady-state hydroisomerization of n-hexane. Steady-state hydroisomerization (n-hexane (10 μl/min) in hydrogen (150 ml/min) at 240 °C) was first carried out for 30 min. The hexane flow was then interrupted and the bed was allowed to empty of adsorbed hexane for 20 min. Five minutes prior to injection the feed stream was then switched to helium (75 ml/min). The PEP image measured following n-$^{11}CH_3C_5H_{11}$ injection is shown in figure 5. The majority of the n-hexane was rapidly dehydrogenated to hexene by the Pt sites at the front of the bed. These hexenes were subsequently immobilized by irreversible adsorption (in the absence of hydrogen) on the Brønsted acid sites and appear as the vertical band in the spectrum. Unreacted hexane continued through the reactor as before. The adsorbed C_6 molecules could be liberated by flowing hydrogen through the bed as confirmed by radio-GC analysis of the trapped products. Small amounts of C_1, C_2, C_7, and C_8 (formed by dimerization and cracking) were also detected.

Apparently, the undesirable metal cracking reactions that occur on freshly-reduced platinum are suppressed by “preconditioning” the surface of the platinum metal during the hydroisomerization reaction. As observed from figure 4, this “preconditioning” involves the deposition of a carbonaceous overlayer that prevents cracking of the hexane. The only function of the “preconditioned” platinum surface is to perform the dehydrogenation of hexane to hexene or the hydrogenation of olefins. This result is consistent with the work by others on model transition metal catalysts, that hydrogenation and dehydrogenation reactions occur on a surface covered by a carbonaceous overlayer [13–15]. The effect of the carbonaceous overlayer may be the reduction of the surface ensemble size available to the cracking reaction; the hydrogenation and dehydrogenation reactions are less structure-sensitive [16].

7. Conclusion

Positron emission profiling provides the ability to measure concentration profiles of molecules labelled with positron-emitting nuclei, such as ^{11}C, ^{13}N, and ^{15}O, inside chemical reactors operating under typical reaction conditions. These profiles, measured as a function of both axial position and time, can then be used as inputs to verify mathematical models describing the various processes occurring. This has been demonstrated for the system n-hexane–Pt/H-zeolites under conditions typical of the hydroisomerization reaction. Data obtained in the absence of reaction (i.e., without platinum) were first measured and used to model mass transport processes in these biporous, packed-bed reactors.

Images obtained under conditions where the injected pulse underwent reaction leading to products that did not exit the reactor demonstrated the need for *in situ* measurement. The initial formation of carbonaceous overlayers formed by hydrogenolysis of hexane on freshly-reduced platinum dispersed in acidic zeolites was measured *in situ* at various temperatures. Such experiments should provide a valuable new tool in the study of transient, initial phenomena so often of importance in heterogeneous catalysis, such as “preconditioning” and deactivation. The role of this carbonaceous overlayer in suppressing subsequent hydrogenolysis reactions was demonstrated.

Acknowledgement

The authors wish to acknowledge the technical assistance of Joop van Grondelle. This work was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Technology Foundation (STW), the Netherlands Organization for Scientific Research (NWO), Eindhoven University of Technology and the Netherlands Institute for Catalysis Research (NIOK).

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