

### Positron Emission Imaging in catalysis

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### Positron emission imaging in catalysis

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#### Abstract

In situ imaging technology developed for nuclear medicine is now being applied to study the kinetics of heterogeneous catalytic reactions under actual process conditions. Minute quantities of molecules (ca.  $10^{-15}$  mol), radio-labeled with positron-emitting isotopes such as  ${}^{11}C$ ;  ${}^{13}N$ ; or  ${}^{15}O$ , are injected as pulses into the feed streams of chemical reactors. Subsequent coincident detection of pairs of gamma photons produced via positron-electron annihilation allows the concentration of reactants, intermediates and products to be mapped as a function of both time and position within the reactor bed. As well as providing qualitative information regarding the mechanism of the reaction under investigation the data obtained can be compared with mathematical models based on the reaction kinetics in order to refine parameters such as activation energies and pre-exponential factors for elementary reaction steps. Since the technique is capable of imaging transient phenomena, information is provided that is not accessible to steady-state techniques.

Keywords: Transient kinetics; Positron emission; In situ imaging; Chemical reactor

#### 1. Introduction

Although the kinetics of heterogeneous catalytic reactions are still most often measured in the steady state there is a growing interest in transient methods since the latter allows one to distinguish directly between various possible reaction mechanisms and to measure the rates of the individual elementary steps [1,2]. Techniques are now currently available which are capable of 'in situ' measurement of chemical species in a quantitative manner. However, the experimental conditions under which these measurements must be performed (e.g. temperature or pressure) often

differ considerably from those which exist under normal process conditions. Thus a question remains as to whether the data obtained can be extrapolated to the real system.

Ideally one would like to have a technique which could 'image' the reactor in such a way as to be able to determine both the chemical identity and quantity of all reactants, intermediates and products as a function of time and position under identical conditions of temperature, pressure, flow rate etc. In addition, it is desirable that the probe method does not disturb the reaction i.e. the method should be non-invasive.

Medical research has provided an incentive to develop several sophisticated non-invasive, in situ, imaging techniques. Techniques such as magnetic resonance imaging (MRI) and computed axial

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tomography (CAT) are now widely used diagnostic tools to study structure within the living human. Other techniques based on the detection of emitted radiation from injected radioactive tracers are used to study biochemical and metabolic function.

These techniques have not as yet been widely applied in engineering and catalysis research although interest is growing. Industrial applications of nuclear magnetic resonance have recently been reviewed by Gladden [3]. An emerging field is that of 'process tomography' [4,5]. In this review we will discuss recent applications of one specific type of emission imaging technique, positron emission tomography (PET), to catalysis research. Although PET is now well established as a diagnostic tool for in vivo imaging of the function of human organs, particularly of the brain and the heart [6], it is probably unknown to most researchers outside of the medical community. Thus we have included a brief description of the technique and of the principles upon which it is based.

#### 2. Positron emission

Unstable nuclei that have an excessive number of neutrons, e.g. carbon-14, can emit fast electrons,  $\beta^-$  particles, in order to attain a stable nuclear configuration. Nuclei with insufficient neutrons, such as carbon-11, can emit fast positrons,  $\beta^+$  particles. Both processes are classified as  $\beta$  radioactive decay. In each case, the mass number of the nucleus, A, remains constant but the atomic number, Z, changes.

Positrons,  $\beta^+$  particles, are the anti-matter equivalents of electrons.

Although several positron-emitting isotopes exist, we will be concerned only with the following three in this review: carbon-11 (half-life  $(t_{1/2})=20.4$  min); nitrogen-13  $(t_{1/2}=9.96$  min); and oxygen-15  $(t_{1/2}=$ 2.07 min). Since all of these radioisotopes are short-lived they must be produced on-site. This is normally accomplished by irradiation of an appropriate target material with energetic beams of protons supplied by a cyclotron. For example, carbon-11 is synthesized by irradiating a target of gaseous nitrogen-14 with 12 MeV protons.

The following nuclear reaction occurs:

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

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

During the irradiation process, the highly energetic protons impart large kinetic energies to the target molecules; these energies greatly exceed the bond dissociation energies. As a result, only very simple molecules survive as products. To produce more complex radio-labeled molecules containing positron emitters post-irradiation chemical synthesis must be carried out which incorporates the smaller radiolabeled fragments into the larger framework. Strategies must be developed such that the desired molecule can be produced and separated from other reaction products and reactants within a few half-lives of the radio-isotope. This normally means that one must use a precursor that is only one or perhaps two reaction steps from the desired target molecule [7]. This requirement has not prohibited the synthesis of radio-labeled analogs of complex molecules such as synthetic drugs and drug metabolites [8]. Nor has the need for a dedicated cyclotron overly curtailed the use of this technique. In fact, it has led to the development of small, shielded, semi-automated cyclotrons which are now commercially available [7,9].

#### 3. Positron-electron annihilation

Since the positron is the anti-particle of the electron an encounter between them can lead to the subsequent annihilation of both particles. Their combined rest mass energy then appears as electromagnetic radiation. Annihilation can occur via several different mechanisms: via direct transformation into one, two, or three photons; or via the formation of an intermediate, hydrogen-like bound state between the positron and the electron, called a positronium atom (Ps). The probability of annihilation and the extent to which each annihilation mechanism contributes depends on the kinetic energy of the positron–electron pair, and is negligibly small at high energies.

Positrons emitted during the  $\beta^+$  decay process possess a statistical distribution of kinetic energies ranging from zero to a maximum value,  $T_{\text{max}}$ , which is dependent on the decaying nucleus ( $T_{\text{max}}$ =0.96 MeV for <sup>11</sup>C); the average kinetic energy is equal to 0.4  $T_{\text{max}}$ . The emitted positrons must therefore be slowed down by inelastic scattering interactions with the nuclei and the bound electrons within the surrounding medium to near thermal values before annihilation can occur. The predominant annihilation process for thermalized positrons is via the direct production of two photons. If both the positron and the electron were at rest upon annihilation, conservation of energy dictates that each emitted photon would have an energy equal to 511 keV rest mass energy of the positron or electron. Conservation of momentum would dictate that the two gamma photons be emitted exactly back-toback (i.e. in opposite directions), since the initial momentum of the positron/electron pair was zero.

However, even when the kinetic energy of the positron is zero upon annihilation, the average kinetic energy of the electrons in the surrounding medium is non-zero, typically ca. 10 eV [10]. Thus, the positronelectron pair will on average have a non-zero momentum. The transverse component of the momentum gives rise to a small deviation from the 180° emission angle (full-width-at-half-maximum of the angular spread ca.  $0.4^{\circ}$ ) and to a small energy shift [11]. The longitudinal component of the momentum gives rise to a slight Doppler shift. The maximum energy shift is 1.9 keV [12]. The contribution of other decay mechanisms is rather small when compared with that of two-photon decay; 97% of the positrons emitted via <sup>11</sup>C nuclei are first thermalized and then annihilate to form two gamma photons possessing energies of  $511\pm2$  keV. The emission angle between these photons is  $180^{\circ} \pm 0.4^{\circ}$ . The remainder of the positrons are either annihilated in-flight to form two photons (2%) or via three photon emission (1%) [13]. The importance of the above with respect the detection of these photons and their subsequent use in image reconstruction will be explained below.

#### 4. Detection of emitted gamma photons

The emitted gamma photons are usually detected using scintillation crystal detectors such as sodium iodide (NaI) or bismuth germanium oxide (BGO) in either of two ways [14]:

- In single photon mode in which only one of the emitted 511 keV photons is detected following mechanical collimation using slits, or;
- 2. In coincidence mode two scintillation detectors on opposite sides are used. Only pairs of detected

events which occur within a preset coincidence window (typically less than 50 ns) are counted.

# 5. Imaging of positron-emitting isotopes in catalysis research

As was stated above, this review focuses on the use of positron-labeled molecules and imaging techniques based on their detection. We will therefore only briefly mention the recent use of positrons as analytical probes, so-called positron annihilation spectroscopy (PAS), to study the structure of heterogeneous catalysts.

In PAS spectroscopy a sample is irradiated with either mono- or poly-energetic beams of positrons. By measuring quantities such as: the lifetime of the positrons; the energy distribution of the scattered positrons; or their angular distribution, it is possible to study the electronic properties of a solid's surface or its bulk. The interested reader is referred to recent reviews on this subject [15–17].

The first use of positron-emitting isotopes as tracers in catalysis research was published as recently as 1984 by Ferrieri and Wolf [18,19]. <sup>11</sup>C-labeled acetylene and propylene were employed to monitor the alkyne cyclotrimerization reaction on silica– alumina supported chromium (VI). These authors named their technique positron annihilation surface detection (PASD). The advantages of using a shortlived positron-emitting isotope rather than the longlived beta-emitting isotope carbon-14 (t=5720 years) are:

- 1. The penetrating power of the gamma photons produced is greater than that of electrons. This enables imaging of both the inner and the outer surfaces of the catalyst to be performed. Indeed the penetration of these gamma photons is great enough that detection can be performed through the steel walls of the reactor (half-thickness in aluminum=3 cm; half-thickness in iron=1.1 cm);
- 2. The short half-life leads to high specific activity. A practical catalyst study can be carried out using less than 37 kBq of carbon-11. This corresponds to less than  $6.5 \times 10^7$  molecules or  $6.5 \times 10^{-8}$  of a monolayer coverage for a single-crystal surface. The extremely small quantities of radio-isotope required coupled with the negligibly small

isotope effects result in a very non-invasive technique.

Carbon-11 labeled acetylene (H<sup>11</sup>CCH) was condensed in vacuo together with propyne onto the chromium catalyst surface. Single annihilation photons were collimated and detected using a sodium iodide scintillation detector. The aromatic products (benzene, toluene, xylenes) desorbed from the surface were analyzed using radio gas chromatography. It was found that the selectivity varied with the acetylene– propylene distribution at monolayer alkyne coverage. Calculation of modeled xylene yields as a function of the acetylene distribution rate resulted in distribution curves that were nearly identical with the experimental data [18,19].

More recently Baiker and coworkers [20] used <sup>13</sup>N-labeled NO to investigate the selective catalytic reduction (SCR) of NO by NH<sub>3</sub> over vanadia/titania at very low reactant concentrations. Concentrations of  $5 \times 10^{-9}$  ppm <sup>13</sup>NO were used (10<sup>11</sup> times lower than those typically used). Again only single annihilation photons were detected by NaI scintillation detectors placed after the reactor bed. The reaction was shown to be first-order in NO. The calculated activation energy was 37 kJ/mol, which was in fair agreement with that measured by more conventional methods (43 kJ/mol).

#### 6. Positron emission tomography (PET)

As mentioned above, PET is now well established as a diagnostic technique in nuclear medicine providing three-dimensional (3D) images of the distribution of radio-labeled molecules within living human organs. Medical PET detectors normally employ one or more rings of small scintillator detectors. The NeuroECAT tomograph for example consists of eight detector banks arranged in an octagonal pattern. Each bank contains eleven BGO scintillation detectors. Individual detector elements in opposing banks are hard-wired to form coincidence pairs. By coincident detection of the two emitted gamma photons the position of the annihilation event can be located along a fixed chord between the two detector elements. As pointed out above, the annihilation position is somewhat different than the original position of radioactive decay since the positron must first be slowed down. This stopping distance determines to a large extent the maximum attainable spatial resolution of the technique and is dependent on the energy of the positron and on the density of the surrounding medium. For 0.4 MeV positrons (average kinetic energy of positrons emitted from <sup>11</sup>C) in a medium with a density of 0.5 g/ml (as a zeolite) this corresponds to ca. 3 mm [13].

During a scan the tomograph is rotated about an axis parallel to the subject and is linearly translated along the same axis. In this manner photons emitted over  $360^{\circ}$  in the plane of the detectors can be recorded. Using tomographic reconstruction techniques the data can be used to map the distribution of the positron emitter in a slice through the subject. Time is required for rotation and translation of the tomograph and to acquire sufficient coincident events for adequate measurement statistics. As a result, PET spectra generally require scan times of the order of 10-15 min, during which time millions of coincidence events will be collected by the scintillator elements [7], thus enabling a full 3D reconstruction of the imaged object to be produced.

Spatial resolutions of 8.5 mm × 8.5 mm in-plane and 13.5 mm in the axial direction can typically be achieved with the NeuroECAT tomograph. Current 'state-of-the-art' PET detector technology based on BGO block-detectors is capable of achieving an intrinsic spatial resolution between 3 and 4 mm in each direction [21]. Significant advances in small-scale 3D PET detectors suitable for applications such as imaging of small-scale anatomies of laboratory animals during drug trials have recently been reported [22,23]. For example, a MicroPET detector has been developed by Cherry at UCLA which incorporates smaller scintillation crystals of lutetium oxyorthosilicate which can be read out by optical fibres coupled to a multichannel phototube consisting of 64 individual elements. This results in: a decreased detector size; an increased spatial resolution; and a greatly reduced cost. The MicroPET is capable of resolving structures as small as a sesame seed, ca.  $6 \text{ mm}^3$  (a 10-fold improvement in resolution over conventional scanners) at an estimated price of \$300 000 (US) (less than 1/5 the cost of conventional PET systems) [24]. Such increases in performance and reduction in cost will undoubtedly lead to an increase in non-medical applications of this technology.

#### 7. Non-medical applications of PET

Application of PET to problems of industrial interest has occurred only recently. To date there remains only one facility world-wide that is dedicated to such studies. Workers at the University of Birmingham in the UK have developed a so-called 'position camera' to image flow patterns by conventional tomographic reconstruction and by tracking of a single tracer particle, positron emission particle tracking (PEPT). [25] Physical processes such as powder mixing in a ploughshare batch mixer [26] and particle motion within a fluidized bed [27] have been studied.

The first application of PET to the study of chemical reactions was conducted by Jonkers and coworkers [28,29]. These pilot experiments were performed at the State University of Gent, Belgium, using a commercial PET-camera designed for medical imaging, the NeuroECAT tomograph described above. The objective was to show that PET could be used to obtain images of a reaction occurring within a tubular, plug-flow reactor operating under normal process conditions and that data could provide information for subsequent modeling of the reaction kinetics.

Model automotive exhaust catalysts of Pt- and Rhloaded CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> were used in these experiments. Minute pulses (ca.  $10^{-15}$  mol) of radio-tracers such as <sup>11</sup>CO, <sup>11</sup>CO<sub>2</sub>, <sup>13</sup>NN, <sup>15</sup>OO, C<sup>15</sup>O and C<sup>15</sup>OO were injected into the feed of the reactor operating under steady-state conditions. Since the residence times of the radio-tracers were of the order of 10-500 s there was insufficient time to produce a complete 3D PET image. Instead a so-called 'injection monitor' option was used to record the arrival of the pulse at various planes perpendicular to the reactor axis. In this mode the tomograph was held stationary and coincident events were registered between individual detector elements in one pair of opposing banks at 1.2 s intervals. The result was therefore a 1D image of the pulse showing the average number of detected counts within 21 equidistant 1.1 cm segments along the axial direction at time intervals of 1.2 s. The constraint to onedimension was not critical since the experimental conditions were regulated such that plug-flow existed.

By calibration of the tomograph using a <sup>22</sup>Na line source the quantitative relationship between the detector response (counts/s) and the amount of radioactivity within a linear element (Bq/cm) was established. Since the radioactivity was proportional to the number of the radio-emitters present, the total concentration of radio-labeled reactants, intermediates and products was determined as a function of distance along the reactor axis and time.

In order to relate the PET data obtained with the chemical reactions occurring, transient kinetic modeling was then performed. Since experiments were performed in a manner such as to be kinetically rather than diffusion limited, molecular transport was not included. Arrhenius-type equations for both the forward and reverse directions of each elementary step (adsorption, surface reaction and desorption) were included along with the appropriate mass balance equations. Parameters such as activation energies, pre-exponential factors and sticking probabilities were taken from literature studies performed under UHV conditions. This system of partial differential equations in time and distance was solved numerically. It was found that fairly good agreement could be achieved between the predictions based on these models using literature values and the PET data. For further details concerning the mathematical modeling of this data the reader is referred to the original papers and to the review by Van der Linde et al. [30].

A facility has recently been built at the Eindhoven University of Technology whose main objective is to apply positron emission imaging to the study of physical and chemical processes which occur within a catalytic reactor under practical operating conditions. The project is a collaborative effort between the Departments of Chemical Engineering and Technical Physics and the Department of Chemical Engineering at Delft University of Technology. The university's 30 MeV AVF cyclotron is used to prepare the positronemitting nuclides: <sup>11</sup>C; <sup>13</sup>N and <sup>15</sup>O. Building on the initial successes of Jonkers et al. [28,29] the aim of this project is to extend the scope of this technique to catalytic reactions involving molecules more complex than the diatomic and triatomic molecules made previously.

#### 8. Positron emission profiling (PEP) detector

As mentioned above the minimum sampling time required to obtain a 3D PET image is too long relative to the residence time of the radio-labeled pulse; only



Fig. 1. Photo of the positron emission profiling (PEP) detector.

1D images can be obtained. Rather than use a costly 3D scanner to measure this data it was desirable from both a cost and a performance standpoint to develop and construct a positron emission detector that was specifically tailored to the measurement of activity distributions as a function of time along a single, axial direction, i.e. to design a detector specifically tailored for studies in tubular reactors. Such a detector has been developed and is called a PEP detector to distinguish it from its 3D parent [31].

The PEP detector is shown in Fig. 1. It has been designed to be flexible so that 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 (upper array labeled A) each and is mounted horizontally with the reactor

and furnace placed between the upper and lower arrays. Each detection element consists of a BGO scintillation crystal (labeled C) coupled to a photomultiplier (labeled B). The eighteen detection elements are situated in a frame which allows adjustment of the overall detector dimensions if required. An aluminum tube (labeled D) is shown in place of reactor and oven.

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, by a detection pair 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 [ $(2\times9)-1$ ] unique, equidistant positions along the cylindrical axis. The coincidence time window is normally set between 30 and 50 ns since the time resolution,  $\tau$ , has been determined to be  $19\pm1$  ns [13] and  $2\tau$  is generally considered to be an appropriate criterion for determining coincident events [32]. It should be pointed out here that the lifetime of an emitted positron is dependent upon the surrounding medium (the basis for positron annihilation lifetime (PAL) spectroscopy mentioned above, see [15–17]). The lifetime of a positron in a solid is dependent on the electron density of the solid; in a zeolite the lifetime of a positron is on the order of 2 ns [13].

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 [31].

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 [13] which 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 can be as high as 35% [13]), 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 (only 28% FWHM) this window is quite large (350–700 keV). The angular resolution was found experimentally to be  $0.5^{\circ}$  [33]. As a result of the above experimental limitations of the detector, effects such as Doppler energy shifts described above have no discernible impact on the PEP images measured.

In summary, the above detection principle can be employed to obtain profiles of the average concentration of all radio-labeled 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.

## 9. Applications of positron emission profiling (PEP)

The PEP technique has been used to study the adsorption of alkanes in zeolites at elevated temperatures, ca. 230°C [34]. Used in this manner, these experiments are a modern version of the pulse gas chromatographic technique which was developed in the late 1950s and the early 1960s and is an extension to the 'tracer pulse GC method', since the PEP method is also capable of in situ measurement of the pulse as mentioned earlier. 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.

The heat of adsorption of *n*-hexane on H-mordenite, 67 kJ/mol, was measured from the dependence of the retention time of a pulse of  ${}^{11}\text{CH}_3\text{C}_5\text{H}_{11}$  at temperatures between 150°C and 230°C. In addition, the fractional surface coverage of *n*-hexane was determined as a function of hexane partial pressure at these elevated temperatures. The temperatures are typical of those used for application of the zeolite in reactions such as hydroisomerization. It was observed that the surface coverage of the zeolite remains large, even at these temperatures.

At this point we feel that, for completeness, we should briefly leave our main theme in order to mention another interesting recent application involving positrons and zeolites. Using a positron annihilation lineshape (PAL) technique known as 2D-ACAR (angular correlation of annihilation radiation), Huang et al. [35,36] have used positrons to the measurement of the acidity of zeolites NaHY and ZSM-5. These authors showed that Bronsted acid sites in the zeolite were capable of oxidizing positronium atoms (Ps), giving back positrons and forming H atoms. This process caused a narrowing of the angular distribution of the collected radiation. They were able to correlate the variation of the experimentally measured lineshape parameter and the acidity of the zeolite sample. Such effects are not observed with the PEP detector due to its much lower angular resolution.

Returning now to PEP imaging of hydrocarbons in zeolites, a method for the production of labeled *n*-hexane ( ${}^{11}CH_3C_5H_{11}$ ) has been developed [37,38]. A nitrogen gas target is irradiated via 12 MeV protons to



Fig. 2. PEP spectra of C-11 hexane on H-mordenite.

form  ${}^{11}CO_2$  which is subsequently reduced to  ${}^{11}CO_2$ over zinc. Labeled CO is then used in a two-step alkene homologation reaction previously developed in this laboratory [39]. <sup>11</sup>CO is pulsed over a vanadiumpromoted Ru/SiO<sub>2</sub> catalyst at 350°C. The temperature is then rapidly reduced to between 90°C and 120°C and 1-pentene is pulsed over the catalyst. Desorptive hydrogenation is then performed. As would be expected for this Fischer-Tropsch process 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,  $10^{-15}$ (approximately 1-3 MBq or mole of  ${}^{11}CH_3C_5H_{11}$ ) is then frozen out ready for injection. If so desired one of the other labeled alkane fractions can be isolated and injected. The radio-labeled fraction is minute compared with the amount of nonlabeled *n*-hexane that is produced as the total amount of the injected pulse is typically of the order of  $10^{-6}$ moles. The production process (i.e. the adsorption of <sup>11</sup>CO on Ru/SiO<sub>2</sub> and the GC separation) can be monitored by NaI scintillation detectors.

Fig. 2(a) shows a typical PEP image obtained following the injection of an <sup>11</sup>CH<sub>3</sub>C<sub>5</sub>H<sub>11</sub> pulse into a hydrogen feed stream (150 ml/min) flowing through a packed-bed reactor containing the zeolite H-mordenite at 150°C. Ca. 200 mg of pelletized zeolite (250- $500 \,\mu\text{m}$ ) was typically used to form a packed column 42 mm in length and 4 mm in diameter. In these spectra, the toal activity measured within each 3 mm segment of the reactor bed is plotted as a function of time. The figure is a 2D representation of the measured activity-time-position surface. The retention time is plotted at various positions within the reactor. The total measured activity (and hence concentration) at that position and time interval is indicated by the gray-scale; with increasing intensity indicating increasing activity. As shown in the figure the pulse progressed linearly through the bed with respect to time. In (a) a pure hydrogen feed stream was



Fig. 3. Constant time cross-sections of Fig. 2(a).

used. In (b) the bed was first presaturated using a mixture of non-labeled *n*-hexane (10  $\mu$ l/min) in hydrogen (150 ml/min) for at least 3 h prior to injection of the labeled pulse into that same mixture. In each case, the peak maximum progressed linearly across the bed with dispersion due to adsorption/desorption and diffusion. The total retention time was 941 s. By comparison, the retention time measured after <sup>11</sup>CH<sub>3</sub>C<sub>5</sub>H<sub>11</sub> was injected into a feed stream of *n*-hexane (10  $\mu$ l/min)/ hydrogen, at the same temperature and total volumetric flow rate, was 49 s (see Fig. 2(b)). The difference in the residence times is due to the different degree of surface coverage [34].

If cross-sections are taken at various constant values along the y-axis of Fig. 2(a) one obtains curves of the measured activity as a function of axial position at constant time. Fig. 3 shows these curves (at 25, 50, 100, 200 and 400 s, respectively). From this figure it is clear that the PEP technique is capable of monitoring the progress of the pulse in situ as a function of position and time. As predicted by theory these peaks are Gaussian in shape and decrease exponentially with respect to both time and position [34]. The broadening of the peaks is due to dispersion caused by adsorption– desorption and diffusion. Diffusion constants for the alkane in the zeolite can be determined using the method of moments or by fitting the activity-position-time surface to an analytical solution of a model based on axially-dispersed plug flow [40].

Following measurement of the physical processes above, attention was turned to the chemical processes of alkanes, specifically to *n*-hexane hydroisomerization, occurring on Pt/H-mordenite under similar conditions. Hydroisomerization is generally accepted to proceed via a classical bifunctional mechanism [41] in which platinum is responsible for dehydrogenation of the *n*-alkane to the *n*-alkene. Bronsted acid sites on the zeolite then isomerize the *n*-alkene to the iso-alkene, which is subsequently rehydrogenated by platinum to complete the process.

Firstly, the steady-state hydroisomerization reaction was studied. The same 4 mm diameter tubular reactor was packed using 280 mg of pelletized (250–500  $\mu$ m) of a 2.0 wt% Pt/H-mordenite catalyst. Following a 3 h reduction in flowing hydrogen (150 ml/min) at 400°C the reactor was cooled to 230°C and a feed mixture of *n*-hexane (10  $\mu$ m/min)/hydrogen (150 ml/min) was begun and allowed to reach steady state (more than 8 h on stream was allowed). The steady-state conversion was measured to be 19%. At this point, an injection of C-11 labeled *n*-hexane was made and the PEP spectrum was recorded. The spectrum obtained (not shown) was remarkably similar to that measured previously on H-mordenite under similar conditions (shown in Fig. 2(b)). This behavior arises because of the fact that under the experimental conditions employed, diffusion within the macropores of the catalyst pellets controls the measured spectrum and since the adsorption/desorption behavior and the effective axial dispersion coefficients of n-hexane, 2methylpentane, and 3-methylpentane are very similar, no chromatographic separation could be observed within such a short column [42].

The behavior of the steady-state *n*-hexane hydroisomerization reaction on Pt/H-mordenite is fundamentally different from that observed by Vonkeman et al. [29] with the CO oxidation reaction on Pt-ceria/ alumina in that, in the latter, the product, <sup>11</sup>CO<sub>2</sub>, only adsorbed to a minor extent on the alumina surface. It was thus desorbed upon formation and was subsequently rapidly swept away in the gas phase so as not to play a significant role in the resultant 'reaction image'. However, the fact that reacting labeled nhexane and labeled product iso-hexanes both appear in the PEP spectrum does not in principle deter one from modeling the process. Numerical modeling of these data based on the bifunctional reaction mechanism is in progress. Thus far applications of PEP have been discussed in which the object was to understand the behavior of chemical reactions occurring under steady-state conditions. However, the ability of PEP to measure concentration distributions as a function of both position and time with short sampling times also enables it to be used to study in situ processes that are transient and highly spatially dependent. This ability has been exploited to investigate two important phenomena which occur in solid acid catalysis, metal preconditioning and catalyst deactivation [42].

Pt/H-mordenite is highly selective under steadystate conditions towards isomerization although platinum metal is a known 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.

The changes in the state of platinum metal conditioning before and after use as a hydroisomerization catalyst are vividly illustrated by the following series

of experiments. The same Pt/H-mordenite catalyst previously used in the steady-state reaction was freshly reduced via hydrogen reduction at 400°C (150 ml/min) after which the temperature was lowered to 230°C. The PEP spectrum obtained following a pulse of labeled *n*-hexane into the hydrogen stream was very different from that reported previously in the steady state. As shown in Fig. 4(a) the pulse reacted strongly near the front of the reactor bed. Some of the activity then exited the reactor very quickly (within ca. 20 s) and some of the activity remained on the catalyst surface. Analysis of the radio-labeled reaction products by trapping and subsequent GC 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 in Fig. 4(a)).

Fig. 4(a) is an in situ image of *n*-hexane hydrogenolysis on freshly reduced platinum surface sites. The vertical band which appeared at the front of the bed resulted from the formation of a carbonaceous overlayer on the platinum surface. It was shown that this overlayer could be completely removed by hydrogenation during temperature programmed reduction at ca.  $10^{\circ}$ C/min between 230°C and 400°C, as measured by using the total activity remaining in the bed (corrected for radioactive decay). The trapped reduction products were mainly *n*-hexane.

Fig. 4(b) shows constant time cross-sections obtained from Fig. 4(a) at: (a) 10 s; (b) 15 s; (c) 20 s; (d) 25 s; and (e) 30 s. Clearly the *n*-hexane pulse is consumed within the front half of the reactor. At times greater than or equal to 30 s (curve (e)) the cross-sections remained invariant with time. This component is due to the carbonaceous overlayer.

Repetition of these experiments at temperatures between 150°C and 260°C clearly showed an Arrhenius-type dependence of the extent of reaction on temperature.

Quite different behavior was observed when the Pt/ H-mordenite catalyst was first used in the steady-state hydroisomerization of *n*-hexane at 230°C. The reaction was interrupted by stopping the hexane feed and after 5 min the labeled *n*-hexane was again injected into the hydrogen stream. The PEP spectrum obtained was remarkably like that obtained during the steadystate reaction. Analysis of the trapped products revealed only C<sub>6</sub> hydrocarbons.



(a)

Fig. 4. (a) PEP spectrum showing n-hexane hydrogenolysis. (b) Constant time cross-sections of (a).

Apparently, the undesirable metal cracking reactions that occur on freshly reduced platinum are suppressed by 'preconditioning' the surface of the



(a)

(b)



Fig. 5. (a) PEP spectra showing catalyst deactivation. (b) Constant time cross-sections of (a).

platinum metal during the hydroisomerization reaction. As observed from Fig. 4(a) this 'preconditioning' involves the deposition of a carbonaceous overlayer that prevents cracking of the hexane. As we will see from the experiments reported in Fig. 5, 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 [43–45]. 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 [46].

The hydroisomerization reaction must be carried out in the presence of hydrogen in order to avoid loss of activity through 'deactivation'. The following type of experiments is shown to illustrate the details of deactivation of the acid sites. Steady-state hydroisomerization of *n*-hexane over Pt/H-mordenite at 240°C was interrupted by replacing the feed with flowing helium. After 5 min an injection of labeled *n*-hexane was made. Fig. 5(a) shows the PEP image obtained. As shown, rapid reaction near the front of the reactor bed occurred forming products which remained strongly adsorbed. Only a small portion of the pulse passed through the bed. Radio-GC analysis of this fraction revealed mainly unreacted  $C_6$ with small amounts of C1, C2, C7, and C8 hydrocarbons. It was observed that all of the labeled products remaining on the surface could be removed if the temperature was increased to 400°C in flowing hydrogen. Analysis of this fraction revealed mainly  $C_6$  hydrocarbons with small amounts of  $C_1$ ,  $C_2$ ,  $C_7$ and  $C_8$ .

Upon repetition of this experiment at temperatures between 180°C and 260°C the extent of reaction clearly varied from 0% to 100%. These total activity– time–position contours could be approximated via an irreversible reaction of A to B with an activation energy of ca. 80 kJ/mol.

This shows that *n*-hexane is rapidly dehydrogenated by platinum and the resulting hexene molecules adsorb on the acid sites of the zeolite. In the absence of hydrogen they cannot be rehydrogenated and therefore remain adsorbed on the acid sites, poisoning them from subsequent reaction. Dimerization or further oligomerization reactions do not occur to a great extent, since no large fraction of higher and lower hydrocarbons was found. The constant time cross-sections obtained from Fig. 5(a) taken at: (a) 10 s; (b) 15 s; (c) 20 s; and (d) 25 s following injection are shown in Fig. 5(b). Curve (b) clearly shows the two components formed; the irreversibly adsorbed hexenes appear at the front of the bed (at ca. 5 mm) and the unreacted *n*-hexane appears at approximately 15 mm. The latter component continued through the bed whilst the former remained constant ad infinitum (see curves (c) and (d)).

These transient experiments provide the first direct demonstration of the so-called bifunctional reaction mechanism [47,48] proposed for alkane hydroisomerization. Promoting platinum acts as an alkane dehydrogenation and an alkene hydrogenation catalyst. The zeolitic protons protonate the olefins, which then, as predicted by theory [49,50], remain strongly adsorbed (enthalpy of protonation  $180\pm 20$  kJ/mol).

Protonated olefins are found to isomerize. From steady-state experiments we deduced an activation energy of isomerization to iso-hexane of approximately  $135\pm20$  kJ/mol [51]. The protonated, isomerized intermediate remains strongly adsorbed. Further reaction only proceeds in the presence of gas-phase hydrogen. Desorbing olefins then will be hydrogenated by platinum to product alkanes. This is consistent with previous studies which showed that the reaction has a positive order in hydrogen partial pressure in the absence of platinum [52].

#### 10. Summary

In situ imaging technology, developed originally for medical research, based on the detection of annihilation photons resulting from the positron decay of labeled tracer molecules is now being applied to heterogeneous catalytic reactions occurring within tubular reactors under normal process conditions. The technique is sufficiently sensitive such that only minute amounts (ca.  $10^{-15}$  moles) of reactants labeled with positron-emitting isotopes such as  ${}^{11}C$ ,  ${}^{13}N$ , or  ${}^{15}O$  need be injected, making it a highly non-invasive technique.

Although the retention times of a pulse in a research-scale tubular reactor are too short to obtain a full 3D tomographic image using current, commercial PET imaging technology, uni-directional activity

distributions can be measured. If reaction conditions are adjusted such that axially-dispersed plug-flow conditions exist, i.e. radial concentration gradients are negligible, measurement of the distribution of the radio-labeled molecules along the cylindrical axis is sufficient. A new detector has been developed which is specifically designed for this purpose. Called a positron emission profiling (PEP) detector it is capable of in situ measurement of the concentration of labeled reactants, intermediates and products within 3 mm segments along the bed at time intervals of 0.5 s.

Mathematical models based on the rate expressions of the elementary steps of the reaction under study can be developed using literature values for parameters such as: activation energy; pre-exponential factor; and sticking probability. These models can be used to predict the concentration distribution of reactants, intermediates and products as a function of time and position along the reactor bed. By comparison of these predictions with the values measured via PEP, parameters can be refined in order to obtain values under process conditions.

Transient phenomena producing spatially localized product distributions such as metal preconditioning and catalyst deactivation can also be investigated in situ using this technique. Qualitative data gives valuable insight into the reaction mechanism.

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