

Imaging of n-hexane in zeolites by positron emission profiling (PEP)

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Imaging of n-Hexane in Zeolites by Positron Emission Profiling (PEP)

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Positron Emission Profiling (PEP) has been used for in-situ measurement of the surface coverage of H-mordenite by n-hexane, as a function of hexane partial pressure, at the elevated temperatures typically used for hydroisomerization by monitoring the retention time of an injected radio-labelled pulse of n-hexane. The labelled molecules ($^{11}\text{CH}_3\text{C}_5\text{H}_{11}$) were produced via a two-step alkene homologation reaction in which ^{11}C , produced using a cyclotron, was added to 1-pentene. The PEP method described is similar to the "tracer pulse technique" however it has the significant advantage of *in-situ* imaging of the pulse.

1. INTRODUCTION

Positron Emission computed Tomography (PET) is a non-invasive, 3D imaging technique used in nuclear medicine that is capable of quantitatively mapping the concentration of a positron-emitting tracer within a living organ (1,2). In the PET technique probe molecules labelled with short-lived positron-emitting nuclides such as ^{11}C ($t_{1/2} = 20.39$ min.), ^{13}N ($t_{1/2} = 9.965$ min.), and ^{15}O ($t_{1/2} = 2.037$ min.) are injected. The emitted positrons have a kinetic energy distribution up to a characteristic maximum, E_{max} , and are slowed down by electromagnetic interactions. The distance travelled by the positrons in matter depends on both the electron density in the medium and on the kinetic energy of the positron. For example, a positron with a kinetic energy of 1 MeV, such as that emitted by a ^{11}C atom, typically has a range of a few millimeters in a zeolite. Once the positron has been slowed down an encounter with an electron will lead to the annihilation of both particles with the production of two γ -photons. Conservation of energy and momentum dictates that two photons of 511 keV be emitted in opposite directions. These photons can be detected using scintillation detectors. In a PET detector, a ring of scintillators is used for coincident detection. The position of the original annihilation event can be reconstructed via tomography using the positions of the detected photons. The number of coincident events at a given position is proportional to the concentration of the labelled emitter.

Advantages of the PET technique are that the positron-emitting isotopes are chemically indistinguishable from their naturally most abundant isotopes and that their short half-lives give

high specific activities, and thus only very small quantities of labelled molecules have to be injected. In addition, due to their high energy and low interaction cross-section the emitted γ -photons can penetrate steel and thus the technique can be used to monitor processes occurring behind such enclosures. This is an advantage over other isotopic labelling techniques such as "tracer pulse chromatography" (3) which use beta-emitting nuclides eg. ^{14}C ($t_{1/2} = 5730\text{yr}$).

Although the PET technique was developed for use in nuclear medicine, the potential applications to study other processes are obvious. It has recently been applied to engineering-related problems by Bridgewater and coworkers at the University of Birmingham, UK. These authors studied the radial and axial velocity fields in a 5 litre ploughshare batch powder mixer (4,5).

In pilot experiments the PET technique was applied to the study of catalytic systems by Vonkeman and coworkers. Using the cyclotron facilities at the State University of Gent, Belgium, these authors used a NeuroECAT positron emission tomograph (a so-called PET-camera) to study automotive exhaust catalysts. In these experiments, the reactions of ^{11}CO , $^{11}\text{CO}_2$, ^{13}NN , ^{15}OO , C^{15}O , and C^{15}OO were studied over Pt- and Rh-loaded $\text{CeO}_2/\text{Al}_2\text{O}_3$ (6,7). An important result of these studies was that kinetic data, obtained during PET experiments under realistic catalytic conditions, could be modelled using reaction parameters determined under typical surface science conditions.

Baiker and coworkers have recently used ^{13}NO molecules to study the selective catalytic reduction of NO by NH_3 over vanadia/ titania at very low reactant concentrations (8). However, detection of photons was conducted using a γ -detector placed after the reactor.

Continuing from the work of Vonkeman and coworkers, a facility has been built at the Eindhoven University of Technology which makes use of the university's cyclotron to prepare positron-emitting nuclides that can be used to study catalytic reactions under practical operating conditions. Two objectives of this project were: to demonstrate that molecules more complex than the diatomic and triatomic molecules made in the previous study could be isotopically-labelled on-line and used as radiotracers; and to develop and construct a positron emission detector that was specifically tailored to the study of chemical reactions within a tubular reactor.

It was decided to use this technique to study the hydroisomerization of alkanes, specifically of n-hexane, occurring within Pt/ zeolite systems since the zeolite is known to play a significant role in determining activity and product selectivity. Although a large body of data and many theories currently exist, the exact nature of this role is still not known. It is clear however that processes such as adsorption/desorption and diffusion play a key part. It has been proposed that the intrinsic Bronsted acid strength of the zeolite proton is solely a function of the Si/Al ratio and that the differences in observed reactivity are due to differences in the heats of adsorption of the alkane on different zeolites (9). Zeolite structure has also been postulated to play a significant role (10).

Before in-situ studies under reaction conditions can be performed, ie. on the Pt-containing zeolites, it is necessary to first study the adsorption-desorption and diffusion processes occurring on the zeolite alone under similar experimental conditions. Here we report the results of experiments in which carbon-11 labelled n-hexane was used to study the n-hexane - H-mordenite system.

The PEP experiments described here represent a modern version of the pulse gas chromatographic technique which was developed the late 1950's and the early 1960's and 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 adsorbable gas through a column packed with the adsorbent of interest. Using these techniques one can measure physicochemical properties related to adsorption and diffusion processes. Using the fundamental equations of chromatography it can be shown that the retention time of an adsorbable gas, t_a , is related to an "equilibrium constant" K by the relation:

$$t_a = \frac{x}{u} \left[1 + \left[\frac{1-f}{f} \right] n_e K \right] = \frac{x}{u \beta} \quad (1)$$

where x = distance, u = gas velocity, f = void fraction of the bed, and n_e is the concentration of the sites available to the pulse. Using the Henry's Law approximation, $n_e = n_0(1 - \theta_{st})$

where n_0 is the total concentration of adsorption sites and θ_{st} is the fraction of sites covered during presaturation.

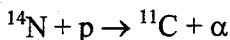
Greene and Pust (11) realized that by assuming that $K \gg 1$ and utilizing the temperature dependence of K that the logarithm of the retention time is linearly related to the absolute temperature. Thus from the slope of the plot of \ln (retention time) versus $1/T$ one can experimentally obtain the heat of adsorption.

We have employed this procedure to calculate the heat of adsorption of n-hexane on H-mordenite by measuring the retention time of $^{11}\text{CH}_3\text{C}_5\text{H}_{11}$ at temperatures between 150°C and 230°C at 10°C intervals. In addition, the fractional surface coverage of n-hexane, θ , in an atmospheric flow of hexane as a function of hexane partial pressure at these elevated temperatures, have been measured. The temperatures are typical of those used for application of the zeolite in reactions such as hydroisomerization.

2. EXPERIMENTAL

2.1. Production of Carbon-11 and labelling of n-hexane ($^{11}\text{CH}_3\text{C}_5\text{H}_{11}$)

Carbon-11 is produced using the Eindhoven 30 MeV AVF cyclotron by irradiating a target filled with 99.999 % pure N_2 gas under 4 bar pressure with 12 MeV protons. The following reaction occurs:



Sufficient oxygen impurities exist in the target to convert all of the carbon-11 to $^{11}\text{CO}_2$. After irradiation of the target for 25 minutes approximately 300 MBq of activity (approximately 10^{-12} mole of $^{11}\text{CO}_2$) is produced. The $^{11}\text{CO}_2$ gas is then flushed from the target using a nitrogen carrier gas and passed through a tubular reactor containing zinc at 380°C where it is reduced to ^{11}CO . The ^{11}CO is then transported to a radiochemical laboratory via a 35 m long teflon tube. The entire process is controlled remotely.

Carbon-11 labelled n-hexane ($^{11}\text{CH}_3\text{C}_5\text{H}_{11}$) is produced using a two-step alkene homologation reaction previously developed in this laboratory (12). ^{11}CO is pulsed over a vanadium-promoted Ru/SiO_2 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. Descriptive hydrogenation

between 90°C and 120°C and 1-pentene is pulsed over the catalyst. Descriptive hydrogenation is then performed. As would be expected for this Fischer-Tropsch process a range of alkanes is produced from C₁ to C₆. The procedure has been optimized for n-hexane production and the maximum selectivity for n-hexane at 120°C is 15 % (13,14). The hydrocarbons are separated by a process of freezing, flash-heating and gas chromatography. The desired product, n-hexane, is then frozen out ready for injection. At the present time, approximately 1-3 MBq of activity (approximately 10⁻¹⁵ mole of ¹¹CH₃C₅H₁₁) is produced. 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 is monitored by NaI scintillation detectors, ie. the adsorption of ¹¹CO on Ru/ SiO₂ and the GC separation.

The entire labelling procedure from ¹¹CO to ¹¹CH₃C₅H₁₁ can be carried out in approximately 30 minutes. It should be borne in mind that ¹¹C decays with a half-life of 20 minutes. In order to optimize the number of experiments that can be performed, irradiation of the nitrogen target to produce ¹¹CO for the next experiment is performed during the n-hexane production process. In this way experiments can be performed at 45 minute intervals.

2.2. The Positron Emission Profiling (PEP) Detector

A positron emission detector has been designed and constructed (15). The detector is unique in that it is designed specifically for studies in tubular reactors. As experiments are carried out under hydrodynamic plug-flow conditions, concentration gradients will only occur along the axial direction of the reactor. Thus measurement of the activity distribution as a function of time is only necessary along this axis. The detector was therefore designed to optimize the measurement of the activity profile in one direction only, and hence we have chosen to call this technique Positron Emission Profiling (PEP) in order to distinguish it from the 3D PET technique. The detector reconstructs the position of the positron-emitting isotopes in one direction by coincident detection of the two photons emitted in opposite directions during the annihilation event. It was 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 cm and 50 cm and diameters of up to 25 cm.

The detector consists of two arrays of nine independent detection elements each. The detector 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 which allows adjustment of the overall detector dimensions as necessary.

The spatial resolution of the detector is 3.0 mm which is comparable to state-of-the-art 3D PET detectors and is near the theoretical limit of the spacial resolution governed by the range of the positrons under study. Temporal information is obtained by collecting data during a fixed sampling period. A minimum sampling 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. In order to reduce errors resulting from the detection of Compton scattered photons, which lead to anomalously positioned annihilation events, energy selection of the photons is also employed.

2.3. The Plug-Flow Reactor:

H-mordenite (Si/Al = 10) was obtained from Exxon Corporation and used without further treatment. The zeolite was pressed into disks which were subsequently broken into smaller pieces and sieved. Particles of between 250 and 500 μm were used in order to avoid pressure drop across the reactor. H-mordenite particles were poured into a tubular quartz reactor (internal diameter = 4.0 mm) until the bed reached 42 mm; typically 200 mg of zeolite was used. The reactor was placed inside a three-zone furnace designed to have a temperature gradient of less than 0.1°C over its entire length of 40 cm. The zeolite was dried by flowing hydrogen gas through the bed at 400°C at 150 NmL/min for at least 3 hours prior to experiment. Hydrogen flow was controlled via a mass-flow controller. The temperature of the reactor was then reduced to between 150°C and 250°C. For some experiments, the zeolite was then presaturated with non-labelled n-hexane by flowing a n-hexane/ hydrogen mixture through the bed at the desired temperature for at least 12 hours. The total volumetric flow rate of the feed gas was 150 NmL/min. Liquid hexane flow rates between 10 and 30 $\mu\text{L}/\text{min}$ were used. N-hexane flow was controlled via an HPLC pump. The liquid hexane was introduced into the hydrogen stream as a vapour prior to flow through the reactor.

The reactor and furnace were centred between the two horizontally-mounted banks of the PEP detector. The trapped condensed n-hexane sample containing the labelled $^{11}\text{CH}_3\text{C}_5\text{H}_{11}$ was flash-heated and injected into the feed gas via a pulse-valve. The profile of the injected pulse was measured using a NaI scintillation detector placed before the reactor. The peak profiles of the injected pulses were Gaussian in shape with a full width at half maximum (FWHM) of 1 second. As stated above, the total amount of the pulse was 10^{-6} moles. This amount is less than 1 % of the calculated sorptive capacity of the H-mordenite sample under the experimental conditions.

3. RESULTS AND DISCUSSION

PEP spectra were measured at constant temperature between 150°C and 230°C at 10°C intervals. Figure 1a shows the PEP spectrum obtained on H-mordenite after $^{11}\text{CH}_3\text{C}_5\text{H}_{11}$ was injected into a hydrogen feed stream at 150°C at 150 NmL/min. The Figure is a two-dimensional representation of the activity-time-position surface. The retention time is plotted at various positions within the reactor. The measured activity at that position and time interval is indicated by the grey-scale; the lighter the grey, the greater the activity. As shown in the Figure the pulse moves linearly through the bed with respect to time. The total retention time was 941 seconds. By comparison the retention time measured after $^{11}\text{CH}_3\text{C}_5\text{H}_{11}$ was injected into a feed stream of n-hexane (10 $\mu\text{L}/\text{min}$) / hydrogen, at the same temperature and total volumetric flow rate, was 49 seconds (Figure 1b).

The measured heat of adsorption was 66.7 ± 1.3 kJ/mole. The same value was obtained via microgravimetric adsorption studies (16). We have also measured the heat of adsorption of 2-methylpentane, 68.2 ± 1.3 kJ/mole. This was done by trapping the labelled 2-methylpentane fraction and injecting it rather than n-hexane. From microcalorimetric measurements (17) the following values were obtained for the heats of adsorption on H-mordenite: n-butane (50 kJ/mole), isobutane (52 kJ/mole), n-pentane (59 kJ/mole) and isopentane (61 kJ/mole). Thus the heat of adsorption was also found to be similar for each pair of normal and iso-isomers, with the iso-isomer being some 2 kJ/mole higher.

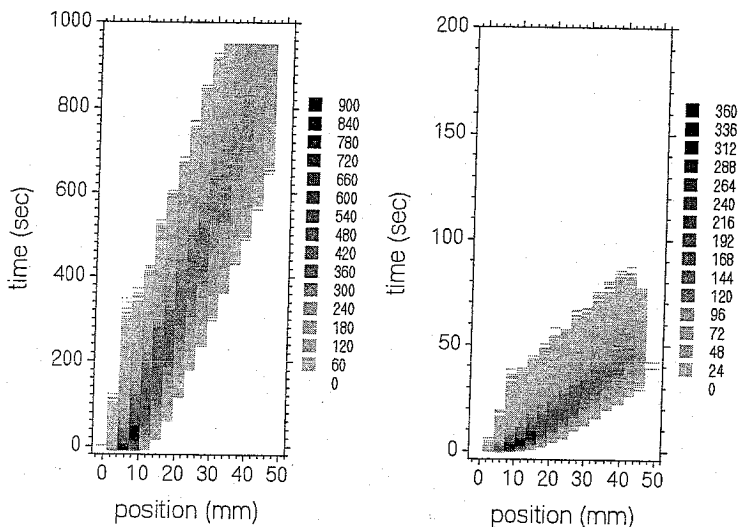


Figure 1: PEP spectrum obtained on H-mordenite at 150°C at 150 NmL/min.
 (a) $^{11}\text{CH}_3\text{C}_5\text{H}_{11}$ injected into a hydrogen feed stream.
 (b) $^{11}\text{CH}_3\text{C}_5\text{H}_{11}$ injection following presaturation using n-hexane (10 $\mu\text{L}/\text{min}$)/ hydrogen.

If we consider the concentration of a pulse of a reversibly-adsorbable gas flowing through a packed bed with an average interstitial velocity of $u = u_0 / f$ the pulse will be dispersed by virtue of axial diffusion characterized by a coefficient, D , and by adsorption/desorption. If we consider the distance along the column axis to be, x , we can write:

$$D \frac{\partial^2 c}{\partial x^2} - u \frac{\partial c}{\partial x} = \frac{\partial c}{\partial t} + \left(\frac{1-f}{f} \right) \frac{\partial n}{\partial t} \quad (2)$$

where c is the gas phase concentration and n is the adsorbed phase concentration. Equation (2) can be solved analytically for an input pulse of volume V to yield:

$$c(x,t) = \frac{V}{f A \sqrt{\pi \beta D t}} \exp \left[\frac{-[x - \beta u t]^2}{4 \beta D t} \right] \quad (3)$$

By differentiating the above with respect to time and equating the derivative to zero, we can obtain the relation for the mean retention time in terms of the pulse maximum. From this

expression it can be shown that the peak maximum progresses linearly across the bed, as was experimentally observed (see Figure 1).

As stated above, using the PEP technique we are able to monitor the progress of the pulse as a function of position and time within the reactor. This is illustrated in Figure 2 by plotting the measured activity as a function of position at different time indices between 20 and 300 seconds at 40 second intervals. The data shown is the same data as in Figure 1(a), ie. from a $^{11}\text{CH}_3\text{C}_5\text{H}_{11}$ injection into a hydrogen feed stream through H-mordenite at 150°C at 150 NmL/min . As shown in the Figure the peaks are Gaussian in shape and decrease exponentially with respect to both time and position, as described by Equation (3).

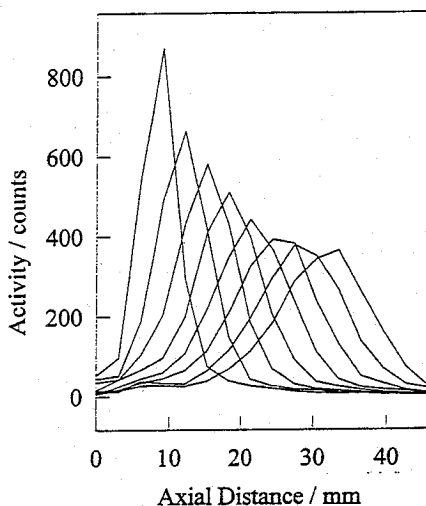


Figure 2: In-situ measurement of the progression of the $^{11}\text{CH}_3\text{C}_5\text{H}_{11}$ pulse through a bed of H-mordenite following injection into a hydrogen feed stream at 150°C at 150 NmL/min . The measured activity at each position is shown for various time indices at 40 second intervals beginning at 20 seconds after injection.

The above experiments in which the heat of adsorption was measured were conducted by injecting the labelled adsorbent into hydrogen only, ie. no presaturation of the H-mordenite was performed. This was done since, in the case of preadsorption, no simple relation exists between the retention times and calorimetric measurements since the latter values are functions of the surface coverage (18).

As described in the experimental section in some experiments the zeolite was presaturated with non-labelled n-hexane by flowing a n-hexane/ hydrogen mixture through the bed at the desired temperature prior to the PEP experiment. The total volumetric flow rate of the feed gas was again 150 NmL/min . Liquid flow rates between 10 and $30\mu\text{L/min}$ were used. Since experiments were performed at atmospheric pressure the partial pressure of n-hexane was 8.4 torr and 25.3 torr respectively. These experiments were repeated at temperatures between 150°C and 230°C . Figure 3 shows a plot of the logarithm of the measured retention time versus reciprocal temperature.

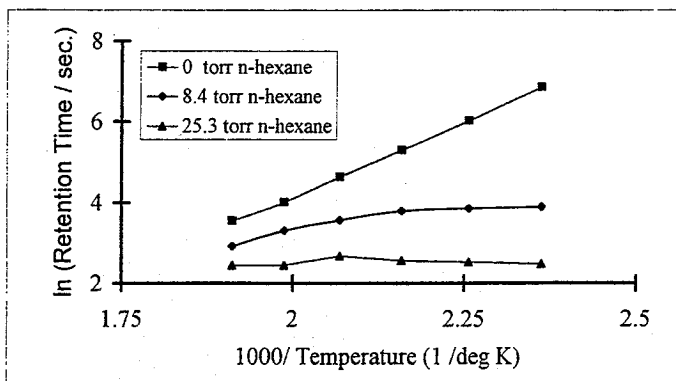


Figure 3. $\ln(\text{retention time})$ versus reciprocal temperature obtained from PEP experiments in which H-mordenite was presaturated with non-labelled n-hexane prior to injection of labelled n-hexane. Partial pressures of n-hexane in hydrogen stream were 0, 8.4, and 25.3 torr. Total pressure = 1 atmosphere. Total flow rate = 150 NmL/min.

From Figure 3 it can be seen that the retention time decreases as the surface coverage increases. Recall that this behaviour was previously shown in Figure 1. The logarithm of the retention time is no longer linear with respect to $1/T$, but rather tends toward a plateau as the temperature decreases. At a hexane partial pressure of 25.3 torr the retention time is the same for all temperatures, i.e. the zeolite is saturated with hexane over the entire temperature range. We can therefore measure the degree of filling of the zeolite, i.e. use the PEP technique to directly measure the adsorption isotherm.

Adsorption/ desorption of alkanes on zeolites is known to follow Langmuir-type behaviour. If we consider a Langmuir adsorption isotherm

$$n = n_0 \theta = \frac{n_0 K c}{(1 + K c)} \quad \text{where again } c \text{ is the hexane partial pressure under steady-state}$$

conditions, then when solving Equation 2, as long as the number of molecules of hexane in the pulse remains small compared to the available empty sites, β then becomes:

$$\beta = \frac{1}{\left[1 + \left(\frac{1-f}{f} \right) (1-\theta) n_e K_H \right]} \quad (4)$$

By substituting Equation (4) into Equation (1) we again have an expression describing the progression of the peak maximum across the bed, for a given partial pressure of hexane.

The experimental data shown in Figure (3) can be used to obtain the surface coverage, θ , at that temperature and hexane partial pressure. The method is as follows. For a given temperature and velocity, the ratio of the measured retention times at two different partial

pressures (ie. for two points that lie on the same vertical intersecting line drawn on Figure 3) is given by:

$$\frac{t_1}{t_2} = \frac{1 + (1 - \theta_1) K_H n_e}{1 + (1 - \theta_2) K_H n_e} \quad (5)$$

assuming that the void fraction, $f = 0.5$. If θ_1 is the surface coverage at a given hexane partial pressure and $\theta_2 = 0$ ie. under flowing hydrogen then, after algebraic manipulation, and assuming that $n_e K_H \gg 1$, Equation (5) becomes:

$$\theta_1 = \frac{t_2 - t_1}{t_2} \quad (6)$$

The following results were obtained via this method.

Table 1
Calculated surface coverages for n-hexane on H-mordenite

Temperature (°C)	θ [p = 8.4 torr]	θ [p = 25.3 torr]
150	0.95	0.99
170	0.88	0.97
190	0.78	0.93
210	0.65	0.86
230	0.50	0.79

From the above it is interesting to note that the surface coverage of hexane is large even at these high temperatures. Similar results for n-hexane on H-mordenite were previously reported by Eberley (16). He also found that the surface remained saturated at comparable partial pressures up to 163°C, the highest temperature reported. Haag has pointed out that alkane sorption levels on zeolites remain large even at high temperatures (19).

4. CONCLUSIONS

It has been demonstrated that molecules more complex than the diatomic molecules made in the previous study could be isotopically-labelled on-line and used as radiotracers. Positron Emission Profiling (PEP) using carbon-11 labelled n-hexane has been successfully applied to measure the heat of adsorption of n-hexane on H-mordenite and to determine the surface coverage of n-hexane on H-mordenite as a function of partial pressure at temperatures relevant to the hydroisomerization reaction. It is noteworthy that the surface coverage remains large even at these temperatures.

The PEP method is capable of in-situ imaging of the pulse within the reactor, which is an advantage over the "tracer pulse method".

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