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Determination of Coke Profiles in Fixed-Bed Catalytic Reactors by a Neutron Attenuation Technique

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Quantitative coke concentration profiles, in fixed-bed catalytic reactors, have been measured *in situ* by the attenuation of a neutron beam aligned perpendicular to the axis of the reactor. Measurements have been made for coking by both parallel and series processes. For the first, the reaction used was the isomerisation of xylenes, while for series coking the dehydrogenation of butene-1 was studied. Results of neutron attenuation measurements were verified by thermobalance and combustion experiments and the excellent agreement obtained demonstrated that neutron attenuation may be used as a *noninvasive* technique for determining coke profiles in fixed-bed catalytic reactors.

INTRODUCTION

In general, the activity of any catalyst will decrease with time on stream. Of the possible deactivation processes, coking is unique because it occurs in side reactions to the main reaction and therefore cannot be completely eliminated for a given feed and a specified catalyst.

If fixed-bed reactors are employed for the catalytic process, a major problem is the distribution of coke, both within the catalyst pellets and within the reactor. Information on this is an important requirement when catalyst regeneration is subsequently carried out, since it is well established that the temperature attained in the bed, during regeneration, is directly proportional to the initial amount of coke present. An uneven distribution of coke can lead to excessive temperature rises in the reactor unless an appropriate regeneration policy is employed. Most of the earlier published work on coke distribution in fixed-bed reactors (e.g., Froment and Bischoff (*1*)), predicts that when the coking reaction is in parallel to the main reaction, deposition of coke will be greatest in the inlet region of the reactor. Conversely, when the coking reaction occurs in series to the main reaction, coke deposition would be expected to be greatest at the reactor exit. These conclusions necessarily follow, since the concentration of the precursor of coke formation will be greatest at the reactor inlet for parallel coking while for series coking the coke precursor (the reaction product) has the highest concentration at the reactor exit. Although recent work by Brito-Alayon *et al.* (*2, 3*) has indicated that these generalisations may be modified under certain conditions depending on the extent of the pellet diffusional resistance and whether adsorption effects are significant, the conclusions reached by Froment and Bischoff are generally accepted for simple reactions under normal operating conditions.

Various methods have been adopted in the past to determine coke distribution in a fixed-bed reactor. The method generally adopted has been to remove pellets from

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known positions in the reactor and to analyse the coke by standard methods, such as oxidation to CO_2 and water. The procedure is well documented by Richardson (*4*). There are obviously problems with this approach, apart from the time-consuming nature of the analysis for the whole reactor. Use of a noninvasive, nondestructive technique would clearly have great merit.

The aim of the present work has been to develop a technique whereby the coke distribution in a catalytic fixed-bed reactor could be determined without disturbing the bed. In order to test the method over a range of axial coke distributions, two reactions were studied. The first of these was the isomerisation of xylenes over a silica-alumina bead catalyst which was found to form coke by Orr and Cresswell (*5*). The second reaction studied was the dehydrogenation of butene to 1,3-butadiene over a chromia–alumina catalyst. Noda *et al.* (*6*) have found that the coking process is consecutive to the main reaction when a hydrocarbon is dehydrogenated over a chromia–alumina catalyst. Initial experiments using neutron radiography were superseded by a neutron counting technique which was found to be more accurate. To check the neutron attenuation results, comparisons were made with conventional methods for determining coke profiles and very good agreement was observed.

THEORY AND DATA ANALYSIS

The neutron transmission method exploits the fact that the slow-neutron-scattering cross section, σ, for a proton is substantially higher than that for any other element likely to be found in a tubular catalytic reactor.

The transmission of neutrons through a sample is given by

$$\frac{I}{I_0} = \exp\left[-t\left(\sum_i N_i\sigma_i^{\mathrm{T}}\right)\right],$$

where t is the specimen thickness, N the number of atoms of species i per unit volume, and σ_i^{T} the total cross section (scattering plus absorption) of atom i.

For two, initially identical, catalyst-filled reactor tubes, one of which has been subjected to coking, the ratio of the transmissions of the two tubes, I_1/I_2, at a specific axial position is given by

$$\frac{I_1}{I_2} = \exp[-tN_{\mathrm{CH}_n}\sigma_{\mathrm{CH}_n}^{\mathrm{T}}],$$

where CH_n is the atomic composition of the coke. Since t, $\sigma_{\mathrm{C}}^{\mathrm{T}}$, and $\sigma_{\mathrm{H}}^{\mathrm{T}}$ are known, then N_{CH_n} can be estimated with a knowledge of n. In the present work a value of $n = 0.5$ was initially selected as a number of experimental studies (*7–10*) have shown this to be a typical value for many cokes. Subsequently, better agreement was obtained between the neutron data and the data derived from thermogravimetry when the directly determined values of $n = 0.55$ and 0.42 for the xylene and butene experiments were used, respectively. The closeness of these values to the original assumption of 0.5 provides the support for the general applicability of the neutron method.

It is important to emphasise that the application of this technique requires that two assumptions are made about the contents of the reactor. The first is that the catalyst packing density is uniform along the reactor which, conveniently in the experiments reported in this paper, can be checked radiographically. The radiographs show quite clearly the overlapping outlines of the individual catalyst pellets.

The second assumption, a more fundamental one, is that the C : H ratio is constant at all points within the reactor and at all times. Separate measurements of this ratio are planned for the future.

The accuracy of the technique is enhanced by a high coke content and by high transmissions before and after coking so that a high neutron count rate is obtained. For the samples used in these experiments 25,000 to 30,000 counts were measured at each point so that the fractional error in I_1/I_2 was ~1%.

EXPERIMENTAL

Equipment. This comprised a feed system, a preheater, and the fixed-bed reactor. The reactor was constructed from Type 316 stainless-steel tubing of 25 mm i.d. and 0.15 mm wall thickness. Two reactors were used in this investigation, one of length 0.6 m being used for the experiments in which xylene was used as the source of the coking while another, 0.8 m in length, was used in the butene experiments. Both reactors were equipped with external heating elements, which were removed before the neutron irradiations were carried out. Temperatures of up to 873 K could be achieved over the whole effective length of the catalyst beds. Temperatures within the bed were measured using six Chromel–Alumel thermocouples of 0.5 mm diameter and the maximum variation of temperature within the bed was found to be ±5°C. These thermocouples were left in place during the neutron experiments.

Two types of reaction were investigated which were known to give different types of coking behaviour. Dehydrogenation of butene-1 was studied over a commercial chromia–alumina catalyst (4 × 4 mm equant cylinders provided by Harshaw) while xylene was cracked in the vapour phase over a silica–alumina bead catalyst (4- to 6-mm beads provided by Kalichemie). For both systems the reactor was brought up to the appropriate temperature (usually 673 K or higher) in a preheated stream of nitrogen. When the correct temperature had been attained the nitrogen stream was switched to a mixture of xylene or butene-1 in nitrogen. The xylene was vaporised prior to being carried into the reactor by the nitrogen stream. The coking operation was continued for various times depending on the amount of coke deposition desired. The coke catalyst bed was then analysed for coke content and distribution using either a thermobalance or the neutron attenuation technique.

Thermobalance experiments. A conventional thermobalance was used to analyse the coke distribution in the catalyst bed. To do this, the coked catalyst bed was divided into sections and a sample of each was oxidised at a temperature of 823 K in the thermobalance using a mixture of 79% nitrogen and 21% oxygen. The water originally present in the catalyst was removed in the initial heating period by passing a nitrogen stream over the sample. When the sample had achieved constant weight at a temperature of 823 K the nitrogen stream was substituted by the 79 : 21 N_2/O_2 mixture of synthetic air. The coke was oxidised and the loss in weight recorded continuously, while the exit gases were passed through infrared analysers to determine the amounts of carbon dioxide and carbon monoxide evolved during the oxidation. The hydrogen content of the coke was determined by measurement of the water produced.

Neutron attenuation experiments. A collimated neutron beam of wavelength 0.48 nm from the DIDO reactor at AERE Harwell was passed through different sections of the coked reactor. The attenuation of the neutron beam allowed the amount of coke deposited to be estimated as discussed above. Initially, neutron radiography using photographic films subsequently analysed densitometrically, was used to measure the neutron attenuation, but the results obtained were insufficiently accurate. Accordingly, a neutron counting technique was adopted in all later experiments which gave much better results; this was used in all experiments reported in this paper. In this method a boron trifluoride counter was employed, the counter being fitted with a ceramic end window. The counter length was 0.3 m and was filled with BF_3 gas at a pressure of 0.92 to 1.0 bar. The exposure time per sample count was 10 s and the average of 8 independent counts was taken for each section of the catalyst bed. The incident beam was masked to a size of 25 × 13 mm and oriented so that the complete cross section of the reactor tube was irradiated simultaneously.

RESULTS AND DISCUSSION

Coking by Xylene

This was accomplished by feeding a premixed xylene–nitrogen stream over a fixed bed of silica–alumina catalyst in a 25-mm-i.d. reactor. The flow rates used were 3 to 4 ml xylene/min in a carrier gas stream of 1000 to 1100 ml/min of nitrogen and the reactor temperatures during the coking period were 457 or 477°C.

The profiles obtained after coking were determined by neutron attenuation with neutron counting using a BF_3 detector as described under Experimental. All profiles exhibited the characteristics of parallel fouling in that the coke deposit was greatest at the reactor inlet, decreasing monotonically with distance toward the reactor exit. Typical profiles are shown in Figs. 1 and 2 for average coke levels of between 1 and 2%. The highest coke levels which occurred at the reactor inlet varied from about 2.2 to 8% by weight.

Figure 1 shows the profile obtained by neutron attenuation using a reactor coking temperature of 457°C. The duration of the period during which coke deposition occurred was 6 h. As can be seen, the coke deposit was greatest at the reactor inlet at about 2.3% and fell continuously with distance along the reactor until at the last point measured, which was 0.6 m from the front of the bed, the coke concentration had decreased to 0.6%.

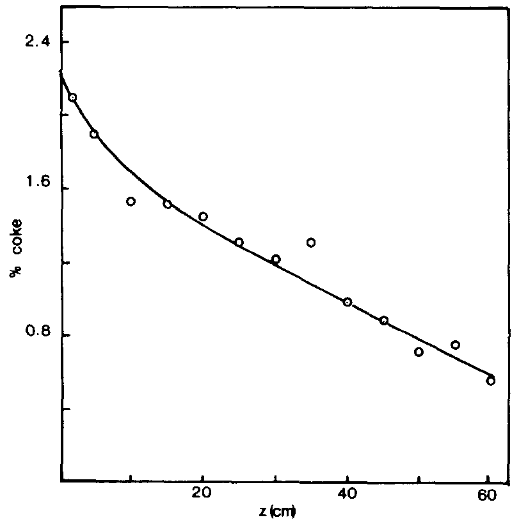

FIG. 1. Experimental coke profiles determined by neutron attenuation. Xylene precursor; inlet temp. 457°C; deposition time 6 h.

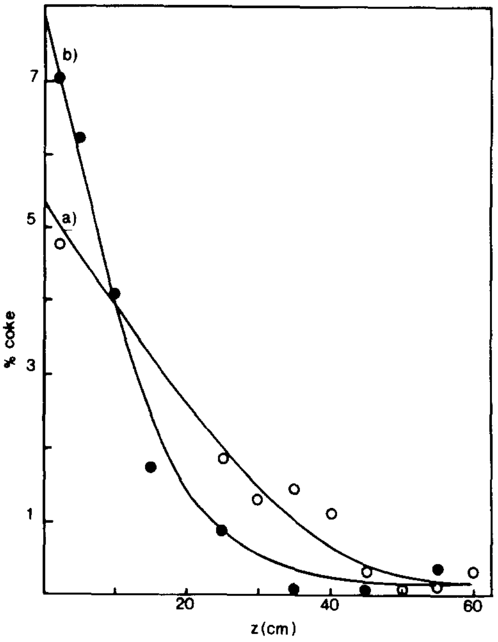

FIG. 2. Experimental coke profiles determined by neutron attenuation. Xylene precursor; inlet temp. 477°C. (a) Deposition time 7 h (○); (b) deposition time 6 h (●).

In the profiles shown in Fig. 2 a higher temperature was used during the coking process. For Fig. 2a the duration of the coking experiment was 7 h. Again the coke concentration decreases from the reactor inlet, but now it falls to almost zero before the reactor outlet is reached. Since the times of coking are not too different in Fig. 1 and Fig. 2a it must be inferred that the temperature increase from 457 to 474°C is the dominant reason for the larger coke deposit in the inlet region of the reactor in the latter case. Interestingly, the average coke levels in both experiments were not too different, ranging from 1.26% in Fig. 1 to 1.95% in the results shown in Fig. 2a. However, the initial coke level was over 5% in the latter case, whereas it was only 2.3% in Fig. 1.

The results shown by Fig. 2b were also obtained at a reactor temperature of 477°C and the time for coke deposition process was 6 h. The drop in coke concentration with distance into the reactor was now more steep than that shown in Fig. 2a, with an initial coke level of 8% being indicated although the average coke level was only 1.65%. In this experiment the coke concentration dropped to a negligibly low value after a distance of 0.35 m from the reactor inlet. The difference in initial coke percentage in Figs. 2a and b is not readily explained and may be caused by the difficulty of aligning the neutron beam close enough to the reactor inlet during the neutron attenuation experiments, thus involving a certain amount of extrapolation of the curves to determine the inlet coke concentration.

The neutron attenuation results described above are consistent and demonstrate the scope of the technique. It is necessary, however, to check the validity of the technique by an independent method. To do this, after a neutron irradiation had been carried out, different sections of the catalyst bed were taken from the reactor tube and analysed by oxidising the coke deposit and determining the weight change using a thermobalance. From this the percentage of coke on the catalyst could be estimated. A comparison of results for neutron attenuation and the conventional analysis is given in Fig. 3, which shows that the agreement between the thermobalance results and those obtained by neutron attenuation measurements is, on the whole, good. The one major exception is the result for neutron counting at the bed exit (0.6 m), where a high value was obtained. Examination of the reactor tube at this point after emptying the tube of catalyst showed that a ring of coke had collected on the reactor walls which could have been caused by liquid xylene condensing at the bottom of the reactor and subsequently coking on the inside of the reactor tube. Whatever the cause, the coke "ring" clearly accounts for the high reading in this section of the coked bed. From Fig. 3 it may be concluded that neutron attenuation gives good agreement with the more orthodox, but time-consuming and destructive, methods of analysis of coke deposits.

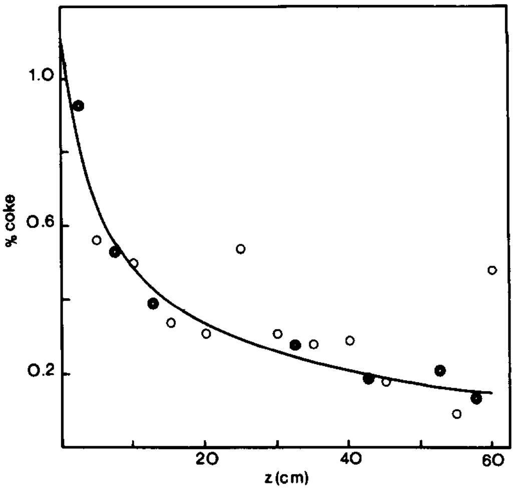

FIG. 3. Comparison of coke profiles by neutron attenuation and weight loss methods. (○) Neutron counting; (●) microbalance.

Coking by Butene

The second chemical reaction used for coking the catalyst was the dehydrogenation of butene-1 over a chromia–alumina catalyst. For these experiments a gas stream containing 52% of butene-1 in nitrogen was passed over the catalyst at a constant temperature of 447°C for durations between 1.5 and 5.75 h.

The first experiment was for a coking time of 1.5 h and the results obtained from neutron attenuation experiments are shown in Fig. 4a. The shape of the coke profile obtained is interesting with a sharp initial rise in coke concentration, followed by an almost constant level of coke deposit of about 1% between the points 0.1 to 0.6 m from the bed inlet. Following this there is a final steep rise in coke concentration to about 4–5% at the bed exit. Although the profile is not regular in shape, the overall increase in coke level from inlet to outlet of the reactor is indicative of series coking, as would be expected from the dehydrogenation of butene. For the results shown in this figure a comparison with thermobalance measurements was not made for all positions in the reactor, only the final section being determined by thermogravimetry. The result for this, which is shown as a half-open circle, lies on the neutron curve and so confirms the high level of coke at the bed exit. The average coke concentration in this experiment was 1.45% over the whole bed length.

When the duration of the coking period was extended to 2 h in a subsequent experiment the results obtained are shown on curve Fig. 4b. The same shape of coke profile was obtained as in Fig. 4a, with a "plateau" region between the inlet section and the final sharp rise in coke concentration at the bed exit. However, the coke concentration in this "plateau" region was now between 2 and 3%, but the length of this "plateau" corresponded approximately to that in Fig. 4a. A final coke concentration of 6% was obtained from these neutron attenuation results, and the average coke concentration along the reactor was 2.5%.

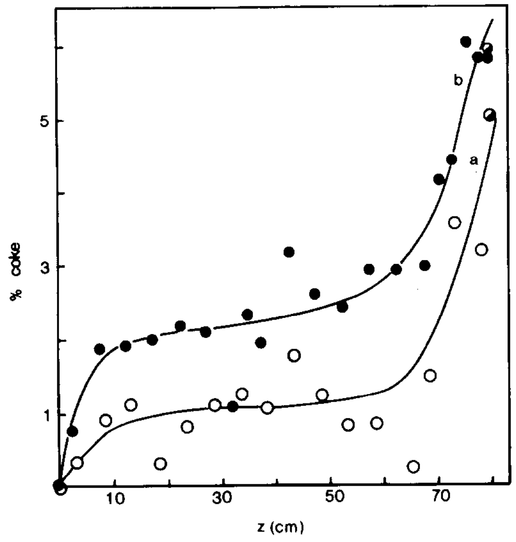

FIG. 4. Experimental coke profiles from butene-1 dehydrogenation; inlet temp. 447°C. (a) Deposition time 1.5 h: (○) neutron counting; (◑) microbalance. (b) Deposition time 2 h: (●) neutron counting; (◑) microbalance.

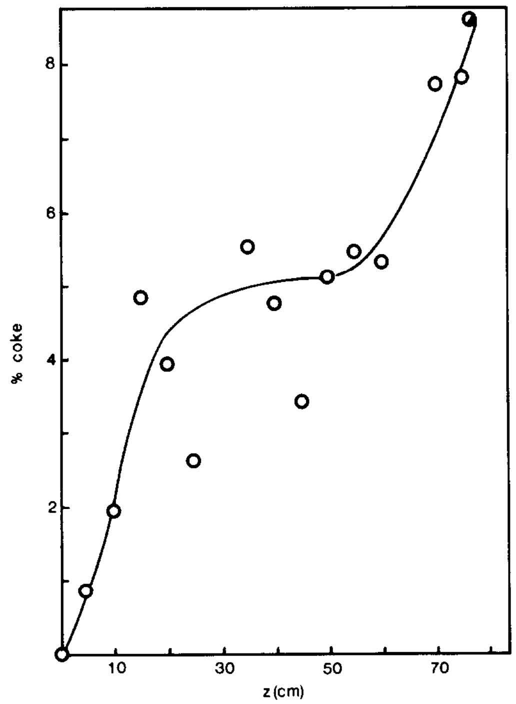

FIG. 5. Experimental coke profiles from butene-1 dehydrogenation; inlet temp. 447°C; deposition time 5.75 h. (○) Neutron counting; (◑) microbalance.

A final butene dehydrogenation experiment was carried out for a time of 5.75 h at the same temperature, flow rate, and concentration as in the two previous experiments. Although there was more scatter in the neutron attenuation results from this experiment (Fig. 5), the curve obtained does show the same general features as those noted above for shorter coking times. A check on the final coke level was made with the thermobalance and the result obtained lies in close proximity to the final neutron attenuation points as shown in Fig. 5. In this coking experiment the average coke concentration was 4.36% while the final coke level attained at the exit of the reactor was about 8–9%.

The gases evolved during the regeneration of the beds after the three butene dehydrogenation experiments were monitored by means of CO and CO_2 analyzers. The total amount of coke in the bed calculated from these readings was in good agreement with the figures obtained from the neutron attenuation results.

Comparison of Results for Coking by Xylene and Butene-1

The above results confirm that the coke deposited from the dehydrogenation of butene-1 over a chromia–alumina catalyst occurs by a consecutive or series reaction. The well-defined "plateau" region occurs in the central part of the reactor, and is followed by a sharp increase in coke concentration. This does not appear to have been reported previously and is at the present time being confirmed, but this feature is itself indicative of the ability of the neutron counting technique to show even a very irregular coke distribution. For xylene, it is clear that coking occurs by a reaction which occurs in parallel to the main reaction.

Perhaps the most notable feature of the coke deposition from butene-1 is that the amount of coke deposited is very dependent on the duration of the coking process. In the xylene experiments, due to difficulties in feeding a sufficient amount of liquid xylene into the system, in order to obtain an adequate coke deposit, variation of the time of coking was not possible to the same extent. For the same reason, as the figures show, the overall levels of coke deposit were less in the xylene experiments compared to those for butene.

CONCLUSIONS

The coke profiles caused by the two extremes of parallel and series coking have been determined by a new noninvasive technique, namely, neutron attenuation. The coke profile for parallel coking was formed by the cracking of xylene while that for series coking was generated by the dehydrogenation of butene-1. Results from neutron attenuation experiments were checked by a conventional gravimetric combustion method with analysis of the product gases and good agreement was found between the two methods.

This new technique is capable of measuring the amount of coke and the coke profile within a deactivated bed of catalyst, without recourse to the tedious and time-consuming task of emptying the catalyst from the reactor tube and doing a conventional combustion analysis on the deposited coke. The method has been shown to work well for laboratory systems and should be capable of further development.

Thus, the experiments described in this paper were performed with a thermal neutron source of intensity 3×10^5 neutrons $cm^{-2}\ s^{-1}$. Portable neutron sources of modest cost and with fluxes of 3×10^2 neutrons $cm^{-2}\ s^{-1}$ can readily be obtained. The collimation and signal to background ratio of these sources would be acceptable for most purposes so that by counting for longer periods and by being prepared to accept lower statistical accuracies on the measured coke concentrations it would be possible to perform this analysis for typical industrial reactors on a manufacturing site. Future work will be directed to the application of such portable sources.

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