NOTE

Determination of C/H Ratios in Coked Catalysts Using a Portable Neutron Source

In a previous paper (*1*), it was shown that a portable neutron source may be employed to measure the coke content of a coked catalyst. In this study, we show how the portable neutron source may also be employed to determine the C/H ratio, i.e., n in CH_n, in the deposited coke.

The importance of hydrogen present in the coke is well recognised since during the catalyst regeneration process, where the coke deposits are combusted, it is the hydrogen component that burns faster and produces additional heat (*2*). This phenomenon is important from two contrasting aspects. Enhancement of the overall heat release from the presence of hydrogen in the coke is beneficial in processes where the exothermic heat from catalyst regeneration is needed to balance an endothermic heat required from the main reaction. However, the presence of hydrogen in the coke may lead to excessive temperature rises in the catalyst during regeneration leading to sintering of the catalyst in extreme cases. Clearly, if the hydrogen content in the coke is known accurately, a more informed strategy for the regeneration process may be formulated. While it is generally known that the n in CH_n usually lies between 0 and 1, no *in situ* measurements for determining n have been made as yet. This is not surprising because of the difficulties involved with such measurements and it is possibly because of this that many modelling studies in the past have assumed the coke to consist of carbon only.

The present study indicates how values of n may be determined from neutron transmission measurements provided that the coke level in the reactor is known. Experimental verification has been obtained for the catalytic dehydrogenation of butene-1 over a chromia–alumina catalyst, but the method should be applicable to a wide range of catalytic reactions where coke deposition is an important factor.

Coke was deposited by passing a butene/nitrogen mixture over chromia–alumina (Harshaw) pellets of 4-mm diameter and 4-mm height. The reactor employed was made of a thin walled (0.15 mm) stainless steel tube of 25 mm inside diameter and 1-m length. The thin wall thickness was required to minimize interference in the neutron experiments. All the experiments reported here were carried out at 723 K with butene concentrations of 35 and 50% in nitrogen and with total inlet gas flow rates of $1.67 \times 10^{-5} \, m^3/s$ and $1.0 \times 10^{-5} \, m^3/s$, respectively. The deactivation time was also varied and for the experiments reported in this work was between 2 and 6 hr.

The portable neutron source used was californium-252 and details of the procedure followed may be found in (*3*). Six successive equal lengths of the coked catalytic reactor were subjected to radiation perpendicular to the reactor by the portable neutron source, the neutron beam being confined to the centre part only, of each section. The neutron count rates were recorded for each section for a total counting time of 15 min. The average of four independent counts was taken for each section. However, the count rates were fairly steady and the variation was less than ±1%. The count rates obtained were in the range 92,000–98,000.

After the neutron experiments, the con-

tents of the reactor were carefully emptied into a perspex tube of slightly larger diameter and length with six precut 25 × 12-mm windows in the centre of each section. Samples of coked catalyst were taken from these windows of each section and analysed for the coke content using a conventional thermobalance technique in which all the coke was removed by combustion at a temperature of 723 K.

The coke content of a given catalyst sample may be calculated from the observed count rates using the relationship (4)

$$C_c = \frac{M \ln(I_0/I)}{\sigma_{CH_n}^T N t \rho_B (1 - \varepsilon)}, \qquad (1)$$

where

C_c = coke content of the catalyst, kg/kg catalyst

M = molecular weight of coke = 12 + n

I_0/I = neutron count ratio of uncoked (I_0) to coked (I) samples

$\sigma_{CH_n}^T$ = total cross section (absorption + scattering) of coke, m^{-2}

$\quad = \sigma_C^T + n\sigma_H^T$

$\quad (\sigma_C^T$ = total cross section of carbon, $m^{-2})$

$\quad (\sigma_H^T$ = total cross section of hydrogen, $m^{-2})$

N = Avogadro constant

t = sample thickness, m

ρ_B = apparent bulk density of the catalyst, kg/m^3

ε = porosity of the reactor bed.

Equation (1) assumes a reference point at zero coke levels.

Upon rearrangement Eq. (1) becomes

$$n = \frac{\sigma_C^T - 12\alpha}{\alpha - \sigma_H^T}, \qquad (2)$$

where

$$\alpha = \frac{\ln(I_0/I)}{C_c N t \rho_B (1 - \varepsilon)}.$$

Equation (2) can be used to determine the value of n in CH_n should the coke content

TABLE 1

n in CH_n from Neutron Method

Dimensionless bed length	Coke %, from microbalance experiments	n in CH_n, from Eq. (2)
0.070	0	0
0.231	1.576	0.14
0.401	2.853	0.36
0.572	2.870	0.38
(0.65)	(2.0)	(0.37)
0.743	2.918	0.36
	(2.25)	(0.37)
0.920	2.931	0.38
	(2.5)	(0.33)

Note. Results shown in brackets were obtained by Santamaria-Ramiro (8) using the thermobalance technique.

of the catalyst be known. Table 1 shows the results obtained from a typical calculation. With the coke values obtained from the thermobalance, Eq. (2) was used to calculate the corresponding n values at the same positions. It can be seen from the table that for dimensionless bed lengths of about 0.4 and greater, a reasonably uniform value of n, i.e., 0.37, is obtained. This is probably due to the high reaction temperature (723 K) and longer deactivation period used in this study, which tends to stabilise the coke levels in the reactor. Similar results have also been reported by Acharya *et al.* (5) where it was shown for the cumene cracking reaction over a zeolite catalyst that the n in CH_n remained virtually unchanged when a temperature of 773 K was used. The n value varied considerably at the lower temperature of 573 K. However, this is not so in the inlet region of the reactor where n was found to be as low as 0.14. This is because this reaction is known to deposit coke by a series mechanism, i.e., the coke forms predominantly from butadiene, a product of the reaction, and since the butadiene concentration is expected to be greater in the outlet region of the reactor, most of the coke forms preferentially in that region (6). The small amount of coke that forms in the inlet region

could arise either because a different coke precursor predominates in this region or because the butadiene concentration is not high enough in this part of the bed. Both these factors could be responsible for low levels of coke deposition in this region.

Additionally, it may be argued that those coke deposits in the inlet region occur during the early period of the reaction and as the reaction progresses, this coke "matures." It has been suggested in the past (7) that as coke matures, it becomes poorer in hydrogen. As is shown in this Note, we have obtained further experimental evidence which confirms this postulate.

It should be noted that the n values obtained from Eq. (2) are in good agreement with those experimentally determined by Santamaria–Ramiro (8) for the same reaction/catalyst system. The n values found were scattered around an average value of 0.42, for dimensionless bed lengths of about 0.4 and greater (8). The hydrogen content was determined by measuring water evolved during the combustion. Due to the low hydrogen content of the coke, only small amounts of water were produced in the combustion and therefore the hydrogen content of the coke was only determined for those samples having higher coke contents, and therefore giving measurable amounts of water during combustion. Since, for this reaction, higher coke contents are found only in the exit region of the reactor, no n values were reported for dimensionless bed lengths less than 0.4.

As mentioned earlier, Eq. (1) has been used in the past to estimate coke levels in catalysts from the neutron count rates measured. This requires information about the coke composition in order that appropriate values of molecular weight and cross section may be used. Since the value of n along the length of the reactor is generally not known, a uniform value of n is usually assumed for the calculations. This can be very crucial in obtaining correct answers from the neutron experiments especially if for a particular process wide variations occur in n. As can

be seen from Fig. 1, the assumption of $n = 0$ (curve 1) or $n = 1$ (curve 3) in Eq. (1) to calculate the coke profile may lead to gross overestimation or underestimation of the actual profile as measured using the microbalance technique (curve 2). It should be noted that lower values of n result in prediction of higher coke contents, while as n increases, the predicted coke levels decrease. Since the values of n remain reasonably constant in the outlet region of the reactor (Table 1), if this value of n is used in Eq. (1) it should be possible to predict coke profiles in good agreement with those predicted from the thermobalance technique. The value of n in the outlet region may be experimentally obtained by analysing a few pellets from this region for hydrogen content. Alternatively, if the coke content in the outlet region is known, it can be used in Eq. (2) to determine n and this value of n may then be used for subsequent calculations. It must be pointed out here that the n value so obtained will not be able to predict coke contents in the inlet region of the reactor, as the actual value of n in this region is about 0.14. Since the assumed uniform value of $n (= 0.38)$ is higher than the actual value of $n (= 0.14)$ in the inlet region, this will result in underestimation of coke levels in this region.

Figure 2 confirms the above arguments for another experiment. The coke content at the exit of the reactor was obtained by the thermobalance technique. Equation (2) was then used to calculate the value of n at this point as $n = 0.5$. This value of n was then used in Eq. (1) and from neutron count ratios, the neutron coke profile was calculated. As can be seen from the figure, reasonably good agreement has been obtained between the two coke profiles, i.e., that for the thermobalance and that from the portable neutron source, except at a dimensionless bed length of 0.2. This is probably due to lower values of n in this region compared to the assumed uniform value of 0.5. As discussed earlier, this results in underestimation of coke level at this point for this particular process.
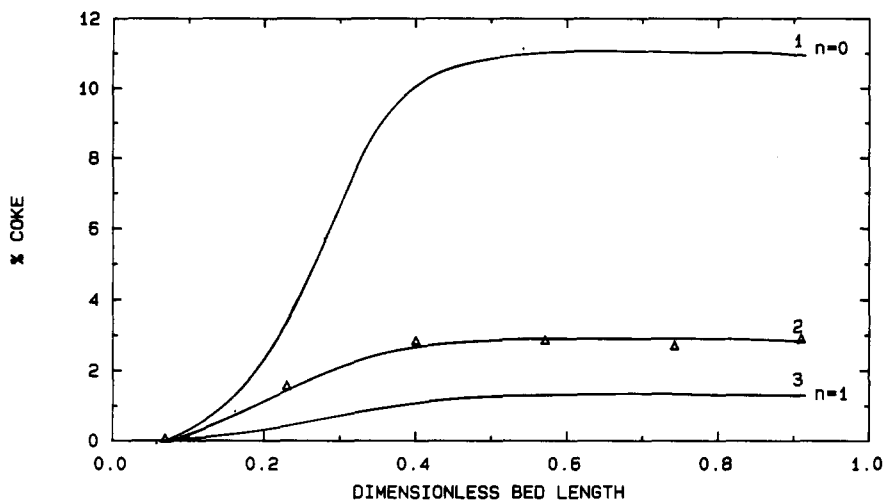
FIG. 1. Effect of hydrogen content of the coke on the coke profile in the reactor: ($\triangle$) microbalance experiments.

It has been reported in the past (7), although no *in situ* measurements have been made, that the hydrogen content of the coke also depends on the deactivation period, i.e., at longer deactivation times the coke has been found to mature which results in loss of hydrogen content. The results obtained by us appear to confirm this theory as can be seen from Table 2 where the n value in CH_n has been obtained for two different operating conditions and two different deactivation times. While the average coke levels increase with the deactivation time as may be expected, the hydrogen content of the coke decreases. For example, at a total flow rate of 1.67×10^{-5} m^3/s, an

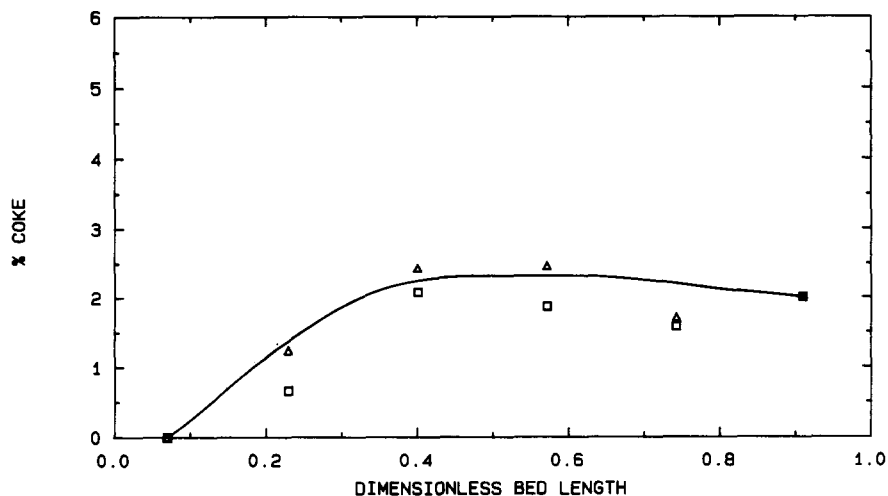FIG. 2. Comparison of coke profiles obtained from microbalance and neutron experiments: ($\triangle$) microbalance; ($\square$) neutron, uniform value of $n = 0.5$.

TABLE 2

Coke Composition for Different Operating
Conditions during Coking

Operating conditions			Deacti-vation time, hr	Average coke levels, %	Average n in CH_n
Feed flow rate, m^3/s	Butene in feed, %	Reaction temp, °C			
1.67×10^{-5}	35	450	4	1.97	0.40
1.67×10^{-5}	35	450	6	2.63	0.32
1.00×10^{-5}	50	450	2	1.65	0.26
1.00×10^{-5}	50	450	3.5	1.94	0.19

increase in deactivation time from 4 to 6 hr resulted in an increase in the average coke deposition from 1.97 to 2.63%. However, the value of the hydrogen content in the coke decreased from 0.4 to 0.32. A similar trend is also observed for the other case at a flow rate of 1×10^{-5} m^3/s and a butene concentration of 50%.

Thus, the present results show that, for this reaction, if the coked sample from the exit of the reactor is analysed for its hydrogen content and the n value so obtained is used in Eq. (1), a reasonably accurate coke profile may be predicted for most parts of the reactor. On the other hand, for a reaction which gives rise to steep coke profiles in certain parts of the catalytic reactor, the use of neutron attenuation can provide an "*in situ*" estimate of the hydrogen content, provided a value for the coke level at the exit of the reactor is established by other means.

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