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Measurement of Coke Levels in Catalysts Using a Portable Neutron Source

In a previous study, Byrne *et al.* (*1*) measured quantitative coke concentration profiles in fixed-bed catalytic reactors *in situ* by the attenuation of a neutron beam aligned perpendicular to the axis of the reactor. The experiments were performed using a collimated neutron beam from the DIDO reactor at the Harwell Laboratory (UK). In this communication, we present some initial results on the *in situ* measurement of coke profiles using a portable neutron source. The advantages of such a source include its transportability and its availability to the nonnuclear industries. However, a possible problem in using a portable source is the low flux of neutrons compared to that of a nuclear reactor.

In order to test the applicability of such a source over a range of coke levels on different catalysts, three reactions were studied. The first of these was the isomerisation of xylenes over a silica–alumina catalyst. The second reaction studied was the dehydrogenation of butene to butadiene over a chromia–alumina catalyst. The third reaction considered was the cracking of cumene over a zeolite catalyst. While the silica–alumina catalyst used was a powder, the last two catalysts were in the form of pellets. The reactions studied also represent different coking processes, i.e., parallel to the main reaction in the case of xylene isomerisation reaction, consecutive to the main reaction in the case of butene dehydrogenation (*1*), and a complex series-parallel coking process in the case of the cumene cracking reaction (*2*).

EXPERIMENTAL

The coke was deposited on these catalysts at 723 K. The amount of coke formed was varied by changing the feed concentration and the time on stream. Nitrogen was used as a carrier gas in all experiments. A conventional thermobalance and combustion technique were used to analyse the coke content of the catalysts. The coked catalyst was then packed in a thin-walled stainless-steel tube of 25 mm i.d. and 0.94 m length. The tube was divided into either three or four sections and each section was filled with catalyst coked to different levels. Before the tube was subjected to the neutron attenuation experiments it was heated to 723 K with nitrogen gas passing through for about 3 h to remove any water vapour and/or adsorbed reactant or products.

The neutron source employed in the present work was californium-252 which emits neutrons by spontaneous fission at a rate of 2.3×10^9 n/sec/mg. The source was surrounded by a moderator material and was stored in a compartment built of boron-loaded resins. The neutrons were collimated using borax collimators and a BF_3 counter was attached to record the neutron beam. The reactor tube was inserted between these borax collimators during the experimentation. The exposure time per sample count was 900 s and the average of four independent counts was taken for each sample. However, the count rates were fairly steady and the variation in successive counts for the same sample was less than ±1%.

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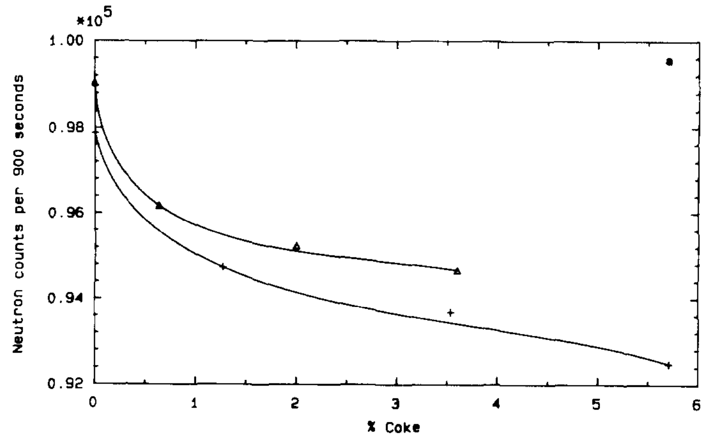

FIG. 1a. Neutron counts versus coke percentage. (△) Pellet of zeolite SDX catalyst; (+) pellet of chromia–alumina catalyst.

RESULTS AND DISCUSSION

The neutron attenuation technique exploits the fact that a neutron beam passes through fresh catalysts more easily than through coked catalysts, i.e., without significant neutron absorption or scattering. As the coke level increases in the catalyst samples, neutron absorption also increases. The neutron count rate measured by the BF_3 counter described previously (*1*) determines the neutrons which are not absorbed or scattered by the material. This implies that at a higher coke level, a lower count rate should be obtained as more neutrons are absorbed compared with that of a sample of lower coke content.

Figure 1a plots the neutron counts obtained in 900 s for different coke contents on a zeolite catalyst. It can be seen from the figure that the count rate of about 99,000 for uncoked catalyst reduces to about 95,000 in the case of 3.6% coke-deposited catalyst. Figures 1a and 1b show similar behaviour for the chromia–alumina and silica–alumina catalysts. It can also be seen from the figures that a nonlinear relationship exists between coke levels and the corresponding count rates, as shown by Byrne *et*

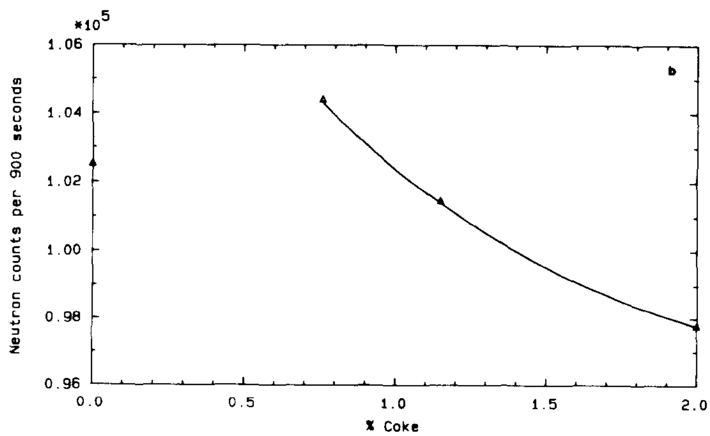

FIG. 1b. Neutron counts on powdered silica–25%-alumina catalyst.

al. (*1*). This is because the transmission of neutrons through a sample is given by (*1*).

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

where t is the specimen thickness, N is the number of atomic species i per unit volume, and σ_i^{T} is the total cross section of atom i. Clearly, the transmission has an exponential relationship with N, which represents the coke level in a given catalyst. This is true for all reactions/catalysts studied in this work. Interestingly, the drop in count rate is maximum between the uncoked catalyst and the catalyst with up to about 1.5% coke. However, this range of coke level, i.e., 0–1.5%, is most useful for cracking catalysts as it represents about the maximum amount of coke formation normally allowed on these catalysts.

It is important to emphasize that the application of this technique requires the catalyst samples to be free of any water vapour as the hydrogen in water absorbs neutrons and causes significant problems in analysing the results. This is particularly true in the case of silica–alumina catalyst, which in addition to containing residual OH groups is known to be extremely hygroscopic. As shown in Fig. 1b, the count rate obtained for uncoked silica–alumina is unusually low and this can only be attributed to the water vapour and the OH groups present. This is despite the fact that the catalyst was heated to about 723 K in the presence of nitrogen prior to neutron experiments. It is interesting to note that the coked silica–alumina samples gave reasonable results (Fig. 1b) and it may then be deduced that the coked samples appear to contain negligible amounts of water. Acharya *et al.* (*3*) have also reported similar behaviour for silica–alumina catalysts.

As mentioned earlier, one of the problems with a portable neutron source could be its low flux compared to that of a nuclear reactor. This would result in a longer counting time in the case of a portable neutron source. For example, the count rate for the portable neutron source used in the present study was of the order of 110 counts/s compared to the DIDO count rate of about 1600 counts/s. It was therefore necessary to take measurements for 900 s in the case of the portable neutron source while in the case of DIDO, a counting time of only about 30 s was necessary in order to obtain reasonable counts so that any associated error due to fluctuations in neutron flux may be neglected. However, our initial experiments tend to indicate that in spite of its lower flux compared to DIDO, the portable neutron source gives the flux at a steady and stable rate which results in more accurate measurements.

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