JOURNAL OF CATALYSIS **156**, 295–297 (1995)

NOTE

Characterization of Carbonaceous Deposits by Temperature-Programmed Oxidation

The reactions of organic compounds on solid catalysts can be accompanied by the formation of heavy by-products which can form a carbonaceous deposit on the surface and cause deactivation. They are of major importance in catalysis research and stimulate considerable interest (1, 2). Temperature-programmed oxidation (TPO) can play an important role in their characterization: it consists of exposing a sample to a flowing O_2/inert gas mixture while increasing its temperature, the amount of carbonaceous compounds oxidized being determined by quantification of the O_2 consumed (3–7) or CO_2 formed (6–11). In this work we have used the former method because of the availability of apparatus to measure O_2 concentration by thermal conductivity.

The problem with measuring O_2 consumption is that one cannot be certain that only CO_2 is formed, and no CO. We report here on the TPO of pure carbon (activated charcoal) in the presence and in the absence of a palladium catalyst, the function of which was to oxidise any CO formed to CO_2.

A carbon sample was located in one arm of a vertical U-shaped quartz reactor between pieces of silica wool, on the top of which was placed a small amount of a 5% Pd/SiO_2 catalyst (1 part to 10 parts of sample): thus the carbon oxides produced passed over the catalyst before reaching the detector. The reactor was fitted with an internal thermowell containing a thermocouple and was heated by a tubular electrical furnace (Stanton Redcroft). The gas stream (5% O_2 in He) passed at 40 ml min^{-1} through a trap containing molecular sieve 5A, through one arm of the conductivity cell, and then through the reactor containing the sample. It then passed through a trap containing solid potassium hydroxide where CO_2 and H_2O formed were retained, through a sample valve, and finally through the other arm of the thermal conductivity cell. After stabilization of the system, the reactor was heated at a linear rate (5 K min^{-1}) and the uptake of O_2 was monitored by the TC cell in conjuction with an integration system. The extent of oxidation was determined at the end of the run by injecting known amounts of oxygen into the gas stream as a calibration standard.

The carbon sample employed was also analysed by thermo-gravimetry in a thermal analyser (Stanton Redcroft) using a 5% O_2/He mixture flowing at 40 ml min^{-1}. The weight of oxidisable carbon in the sample was 96% of the whole, the remaining 4% presumably being inorganic impurities.

Before examining TPO of carbon, the experimental set-up was tested by reducing and oxidising a reducible oxide. A weighed sample of NiO was placed in the reactor instead of carbon (no Pd/SiO_2 catalyst was present in this case). The NiO sample was reduced by temperature-programmed reduction (6% H_2/Ar mixture flowing at 40 ml min^{-1}), cooled to ambient temperature in the H_2/Ar mixture, purged with N_2, and then oxidised under the TPO conditions described above. The O_2 uptake was within 5% of the expected value. The test experiment was repeated with CuO instead of NiO: then O_2 uptake was within 4% of the expected value. This agreement was considered as satisfactory proof of the viability of the set-up and the TPO procedure.

The TPO plots of carbon samples (Fig. 1) showed only one peak in the range 969–1035 K. Expected O_2 uptakes were based on the supposition (i) that only CO_2 was formed, and (ii) that 96% of the sample was oxidisable. The results showed (Table 1) a lower O_2 uptake in the absence of the Pd catalyst than in its presence; the agreement with the expectation in the latter case was excellent. We conclude some CO was formed, but that the Pd catalyst succeeded in oxidising it to CO_2.

We then applied the modified technique, using the Pd/SiO_2 catalyst as described, to estimate the quantity of carbonaceous deposit formed on a 1% V_2O_5/TiO_2 catalyst during its use for the oxidation of *o*-xylene to phthalic anhydride. TPO plots obtained with samples previously treated with an *o*-xylene/air mixture for various times are presented in Fig. 2. The peaks are broader than those for activated carbon (Fig. 1), and they exhibit one or more shoulders which may correspond to the oxidation of various heavy organic compounds on the V_2O_5/TiO_2 surface. The formation of such heavy by-products has in fact been mentioned on several occasions (12–14), but no quantification of them has so far been made. Their oxidation occurs at temperatures lower than those observed for the activated carbon because of their greater dispersion and the effect of the V_2O_5/TiO_2 in catalysing the process. These

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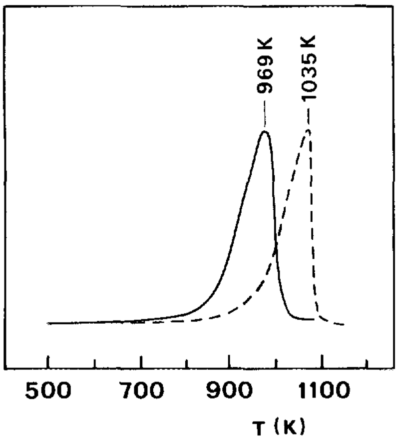

FIG. 1. TPO plots of pure carbon samples: (---) no Pd; (—) plus Pd.

TABLE 1

Temperature-Programmed Oxidation of Pure Carbon Sample

Run[a]	Oxygen consumption (10^{-2} mol O_2 g^{-1}) Observed	Expected[b]	T_{max}(K)
A	7.2	8.0	1035
B	7.9	8.0	969

[a] A, carbon (no Pd); B, carbon plus Pd.

[b] Considering the reaction C + $O_2 \rightarrow CO_2$ and TGA results.

by-products comprise molecules having aromatic rings and are formed by polymerization of intermediate species involved in the oxidation of *o*-xylene.

Figure 3 shows the oxygen consumption obtained by TPO for samples of the 1% V_2O_5/TiO_2 tested under different operating conditions. This initially increased with the time they remained under reaction conditions, but it generally attained a constant level after 1 h. However, at the lowest temperature and contact time, no constant value was reached, although the rate of increase of oxygen consumption declined at longer exposure times. The quantity of carbonaceous deposit thus increases (i) with decreasing temperature and (ii) with decreasing contact time, as both of these factors cause the conversion to decrease, and the literature (12, 14) confirms that these are the conditions under which the deposit is predominantly formed.

Precise conversion of the oxygen uptake into a number of carbon atoms retained by the catalyst cannot be made by this method, as some of it may be employed to oxidise

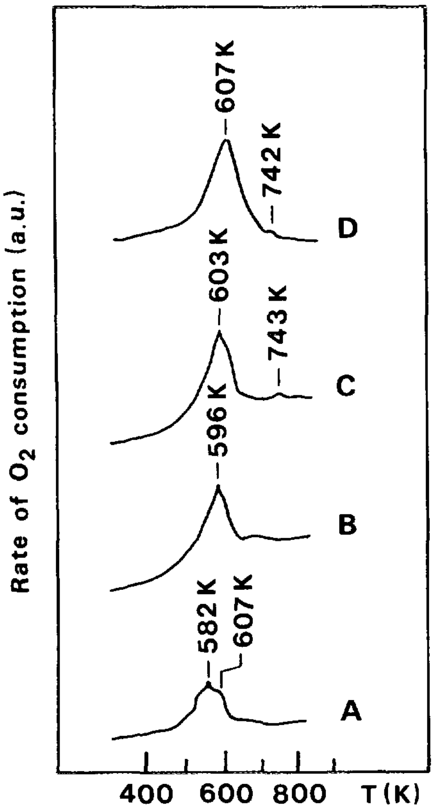

FIG. 2. TPO profiles of 1% V_2O_5/TiO_2 tested for *o*-xylene oxidation at 533 K. Time of exposure under reaction conditions: (A) 0.25 h, (B) 1 h, (C) 2.5 h, (D) 4 h. *o*-Xylene concentration, 0.7 mol%; contact time, 1.6×10^{-5} kg_{cat} dm^{-3} h.

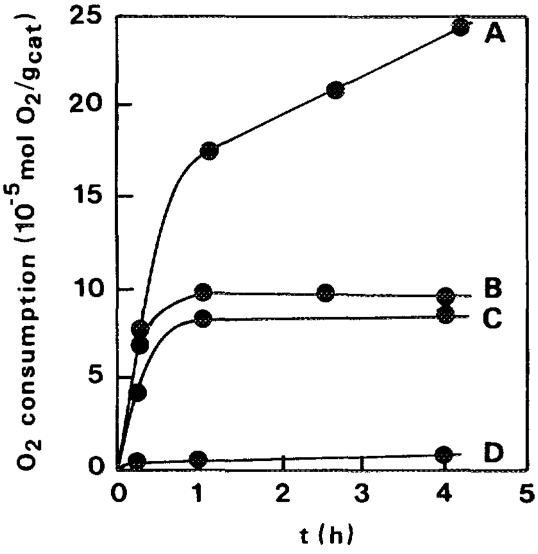

FIG. 3. Oxygen consumption obtained by TPO versus time of exposure to *o*-xylene/air mixtures (*t*) at different temperatures (T_R) and contact times (*W/F*). (A) $W/F = 1.6 \times 10^{-5}$ kg_{cat} dm^{-3} h, T_R = 533 K; (B) $W/F = 1.6 \times 10^{-5}$ kg_{cat} dm^{-3} h, T_R = 613 K; (C) $W/F = 2.3 \times 10^{-4}$ kg_{cat} dm^{-3} h, T_R = 613 K.

the hydrogen atoms in the deposit. However, as we shall show in a paper soon to be submitted, which will supply much more information on the nature and amount of the deposit as a function of operating conditions, the substituent groups on the aromatic rings are at least partially oxidised, and so there may be no more than four hydrogen atoms to every six carbons. Since each carbon uses two oxygens, and each hydrogen only half an oxygen atom, the carbon will account for most of the observed oxygen uptake. The palladium in the Pd/SiO_2 is only 0.0005 mol per mol of activated carbon used, and is probably already oxidised when placed in the reactor. Even with the V_2O_5/TiO_2 samples, which contain less oxidisable material, any further oxidation of the palladium is unlikely to contribute significantly to the oxygen uptake.

The TPO technique, in combination with a catalyst to ensure that only CO_2 is detected, is therefore suitable for determining the quantity of carbonaceous deposits on catalysts.

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Received July 18, 1994; revised June 7, 1995; accepted June 29, 1995

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