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LETTERS TO THE EDITORS

The Photoreduction of Chromium Trioxide on Silica–Alumina Support

Chromium trioxide is reported to decompose only above 180° (*1*). It is even more stable when deposited on alumina, silica, or silica-alumina (*2*, *3*), and this is the form in which it is used as a catalyst. Similarly, we found, for instance, that 2.3% chromium trioxide on silica-alumina kept its typical yellow coloration at 300° and at less than 10^{-4} mm Hg, provided organic material was absent. In the presence of organic material the color turned green at 300° and on evacuation, at 100°; at room temperature the yellow color was maintained even at high vacuum.

On the other hand, when 2.3% chromium trioxide on silica-alumina was dried for 30 min at 300° *in vacuo*, allowed to polymerize ethylene at —23°, and the still yellow solid under argon than illuminated at room temperature by direct sunlight, reduction of chromium trioxide occurred readily.

TABLE 1

	Titration expressed as % CrO_3
Original material	2.3
After	
30 min in sunlight	1.65
60 min in sunlight	1.5
360 min in sunlight	0.8
360 min in dark	2.3

The results (Table 1) show that the reaction is a photoreduction. This reaction could also be observed when the solid was contacted at room temperature with ethylene, *n*-heptane, or acetaldehyde and illuminated; with methane no reaction took place.

The reduction occurred more readily in the presence of a little moisture. When water vapor was added, the photoreduction yielded a brown product containing 0.97% residual CrO_3, compared to a green product containing 1.75% CrO_3 obtained when the "dry" solid was illuminated for the same duration under identical conditions.

We have not found any previous reference to the photoreduction of chromium trioxide in the solid phase.

In aqueous solution hexavalent chromium causes the photooxidation of many classes of organic compounds (*4–8*) among them ethylene (*4*) but not methane (*4*) nor acetaldehyde (*6*). It is now generally accepted that the dichromate ion is the photoactive species in solution (*5*, *7*, *8*). It appears from our results that the mechanisms of the photoreduction of Cr^{VI} in the presence and in the absence of water may be different.

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A Novel Catalytic Method for the Preparation of DPPH and the Application of the Technique to Active Surface Area Studies

We wish to report (i) a novel method using Group VIII transition metals (platinum) and their oxides (platinum, ruthenium, and iridium) for the preparation of the radical, diphenylpicrylhydrazyl (I, DPPH), from diphenylpicrylhydrazine (II) and (ii) the possible application of this technique to the measurement of active surface areas using Adam's catalyst as an example.

A typical reaction procedure utilizes Adam's catalyst prepared by exposing $PtO_2 \cdot 2H_2O$ covered with water to hydrogen at 25°C to facilitate slow reduction to the metal. The water and residual hydrogen gas are then pumped off and the catalyst exposed to oxygen which appears to form a monolayer of chemisorbed oxygen (*1*).

Room-temperature addition of this catalyst to a benzene solution containing (II) liberates the radical (I) readily. The reaction is faster than the conventional PbO_2 preparative method (*2*) and yields a cleaner product. The reaction does not proceed with a prereduced catalyst from which oxygen has been carefully excluded and it would thus appear that reaction does not occur via hydrogen abstraction by the platinum metal. If oxygen is excluded from the hydrazine reagent and the platinum catalyst covered with chemisorbed oxygen, the reaction stops as soon as all chemisorbed oxygen is scavenged. However, the reaction may be restarted immediately by bubbling oxygen into the system. Preliminary indications are that oxygen supply is the only limiting factor in the reaction and thus it is practical to prepare large quantities of the radical quickly and efficiently at room temperature.

The high sensitivity of ESR spectroscopy makes the above reaction suitable for the determination of the number of active sites and, therefore, the active surface area on a catalyst such as prereduced platinum used for isotope exchange reactions. Extensive work has been reported for hydrogen exchange between deuterium oxide and aromatics such as benzene (*3*). The deuteration reaction proceeds smoothly at room temperature on a prereduced Adam's catalyst from which oxygen has been carefully removed; however, the exchange is completely poisoned if the catalyst is exposed to oxygen, i.e., all active sites are combined with oxygen.

When such a poisoned catalyst was reacted with (II) and the amount of (I) generated was compared with a standard DPPH solution, a value of 2.8×10^{18} active centers per gram of catalyst was obtained. Using a figure of 8 Å^2 per oxygen atom, this corresponds to an active catalyst