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Yehuda Haas
Chiya Eden
Hans Feilchenfeld

Department of Physical Chemistry,
Hebrew University of Jerusalem,
Israel

Received November 10, 1966

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 surface area of 0.17 m^2/g. The result is lower than the range obtained for surface area measurement of these catalysts by the carbon monoxide method (*4*). This would imply that the present technique measures either the number of active sites only on an active platinum catalyst or that the rapid reduction procedure used in these preliminary experiments preferentially sinters the catalyst sites to give lower surface areas. These points will be clarified in future experiments where it is intended to use the Hightower and Emmett method (*4*) to achieve higher surface areas by careful reduction of $PtO_2 \cdot 2H_2O$ at 0°C in the presence of copper wire, thus reducing the effect of sintering.

Addition of $PtO_2 \cdot 2H_2O$ to a benzene solution of (II) also generated the radical (I), presumably by self-activation (*5*); however, this reaction was slower than that previously discussed with platinum metal in the presence of oxygen. Even after 40 min at room temperature with platinum oxide, the conversion of (II) into (I) was extremely low, giving surface areas which were only 3% of those obtained on prereduced platinum after several minutes. This result would indicate that oxygen adsorbed on platinum oxide behaves quite differently in the DPPH reaction to oxygen adsorbed on prereduced platinum. A number of Group VIII transition metal oxides ($IrO_2 \cdot 2H_2O > RuO_2 \cdot H_2O > IrO_2 > PtO_2 \cdot 2H_2O$) have been used in this system, however, no correlation is apparent between ease of reduction with hydrogen gas or with their ability to form ESR active radical-ions (*6*).

In future work possible applications of the present active surface area technique to other prereduced oxygen-poisoned active catalysts including evaporated metal films and carbons will be considered.

ACKNOWLEDGMENTS

The authors thank the Australian Institute of Nuclear Science and Engineering (Mr. E. A. Palmer) for continued support. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

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J. L. GARNETT
A. T. T. OEI
W. A. SOLLICH-BAUMGARTNER

School of Chemistry,
The University of New South Wales,
Kensington, N.S.W., Australia

Received November 29, 1966