

thus exhibits considerable cracking activity. The results are of even greater interest in that unsupported molybdenum oxide catalysts have definite cracking characteristics on heptane as unpublished data from this Laboratory show. A typical gas yield from dehydrogenation of heptane on such unsupported molybdenum oxide shows: unsaturates 11%, saturates 47%, hydrogen 41%.

Summary

1. Chromium and molybdenum oxide catalysts admixed with hydrocarbons are highly efficient for the removal of thiophene at 470°. With chromium oxide the greater part of the sulfur input comes off as hydrogen sulfide during the course of passage of vapor, hydrogen being pres-

ent. With molybdenum oxide, on the other hand, only traces of hydrogen sulfide appear during the run and the bulk of the recovered sulfur comes out in the regenerative oxidation.

2. The sulfur from the thiophene has a profound poisoning effect on the aromatization activity of the chromium catalyst, a drop of about 60% in the aromatic yield being observed.

3. The aromatization activity of the molybdenum catalyst is considerably enhanced by the passage of sulfur-containing hydrocarbons. An increase in aromatic yield from 21 to 64% was observed under optimum conditions. Sulfur in excess of the optimum depresses the activity but not to its original value.

PRINCETON, N. J.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Silicon Carbide Electrode

By D. N. HUME AND I. M. KOLTHOFF

It has been claimed by Kamienski¹ that an electrode made of silicon carbide (carborundum) when dipped into a solution gives a potential which is almost independent of the presence of oxidizing or reducing agents. This observation was assertedly verified by Lifschitz and Reggiani,² and the use of silicon carbide as one member of a bimetallic electrode pair in potentiometric titrations has been described by these workers and a number of others.³ In view of the great practical and theoretical importance of such an ideally inert electrode, we have investigated the electrode properties of silicon carbide. The results unambiguously show that a properly made silicon carbide electrode behaves as an ordinary oxidation-reduction indicator electrode like platinum or gold.

Experimental

The electrodes were made from large fragments and single crystals of silicon carbide ranging in color from clear, pale green (almost colorless) to deep blue and jet black. No difference in behavior due to color was observed. A few electrodes were made from rods of pressed Carborundum granules. Most of the material was kindly supplied by the Carborundum Company of America, to which we

express our appreciation for its cooperation. The electrodes were constructed by sealing the crystals or short sections of rod to the open ends of glass tubes by means of de Khotinsky cement. Electrical contact between the inner surface of the crystal and the wire to the potentiometer system was assured by pouring a little mercury into the tube. The behavior of the electrodes in potentiometric titrations was studied by measuring their potential against a suitable reference electrode (calomel or quinhydrone) and comparing it with the potential of a bright platinum electrode in the same solution and measured against the same reference electrode. Potential measurements were made with a potentiometer set-up, using a galvanometer with a sensitivity of 28 megohms.

Titration were made of potassium iodide with permanganate and with ceric sulfate, of ferrous iron with permanganate, of titanous chloride with ferric chloride, and of hydrochloric acid with sodium hydroxide. A typical set of results is shown plotted in Fig. 1. All the results led to the same conclusion, that the silicon carbide electrode behaves as a noble metal electrode, adopting the potential of the solution into which it is placed. In well-poised systems the silicon carbide electrodes almost immediately assumed the potential of the platinum electrode to within one or two millivolts. At the equivalence points they gave pronounced potential leaps, but did not attain the equilibrium values as rapidly as the platinum. This makes possible the use of the platinum-silicon carbide pair as a bimetallic electrode system. The use of this pair is hardly to be recommended, however, because various silicon carbide electrodes gave markedly different potential breaks against platinum.

A few of the electrodes did not behave in the normal manner, but, as Kamienski claimed, they maintained ap-

(1) B. Kamienski, *Z. physik. Chem.*, **A138**, 345 (1928); **145**, 48 (1929).

(2) I. Lifschitz and M. Reggiani, *Gazz. chim. ital.*, **61**, 915 (1931).

(3) (a) Kahlenberg and A. C. Krueger, *Trans. Am. Electrochem. Soc.*, **56**, 201 (1929); (b) J. A. Atanasiu and A. J. Velculescu, *Z. anal. Chem.*, **85**, 120 (1931).

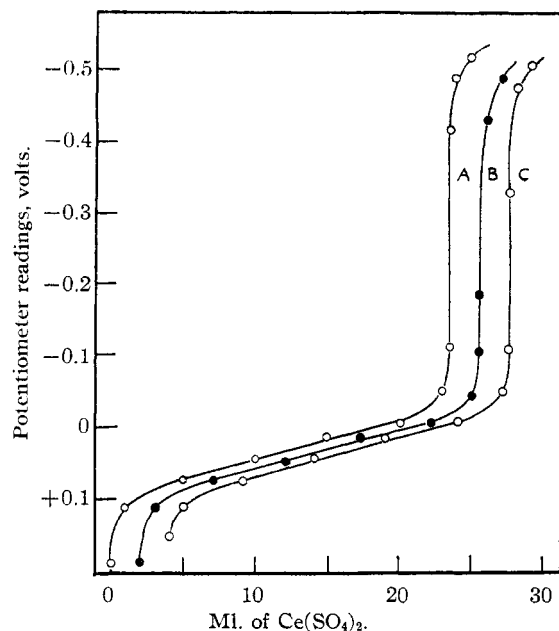


Fig. 1.—The titration of 25.00 ml. of 0.0998 *N* potassium iodide diluted to 100 ml. and made 1 *N* in sulfuric acid, with 0.1062 *N* ceric sulfate. Reference electrode: quinhydrone in 1 *N* sulfuric acid. A, platinum electrode; B and C, two silicon carbide electrodes. The abscissas for B and C are displaced 2 and 4 ml., respectively, to the right for the sake of clarity.

proximately the same potential throughout the titration. In every instance this behavior could be traced to some external cause not a fundamental electrochemical property of the silicon carbide. With single crystal electrodes the deviation was always due to faulty seals or cracks in the glass which permitted the solution to come in direct contact with the metallic conductor (Hg) inside. The same effect was obtained simply by filling a cracked glass tube with mercury and using it as an electrode. With crystals which had a rough surface or many fine cracks and fissures it was very difficult to obtain good seals with the de Khotinsky cement. The electrical resistance of the crystals was found to be quite high, a rather sensitive galvanometer being needed to obtain accurate settings during the titrations.

Since the electrical resistance of the improperly made electrodes was very much less, a worker with an insensitive galvanometer, or a capillary electrometer such as Kamiński used, and not aware of this condition might easily assume the good electrodes to have improper electrical contact with the metal conductor, and so discard them.

The electrodes made from stick Carborundum were at first found to give a constant potential throughout the course of the titration. This was traced to the porous nature of the material, which caused the electrodes to absorb a considerable quantity of the solution by capillary action. The use of a short rod resulted in direct contact between solution and metallic conductor as before. If a long rod were used, projecting far out of the solution so that there was no contact between solution and metallic conductor, the absorption of the original solution still caused an almost constant potential as the titrating agent could reach the interior of the electrode only by slow diffusion. In this respect the long rod behaves like a shielded electrode in the well known differential titration method. The rod electrodes would take the potential of the platinum electrode at the end of a titration if allowed to stand in the solution for several days. By previously soaking the stick Carborundum in melted paraffin, electrodes could be made which did not absorb any of the solution being titrated. These behaved like the electrodes made from single crystals.

Since silicon carbide electrodes are troublesome to prepare, have a high resistance (requiring a very sensitive galvanometer), are sluggish in unpoised systems, and are not to be relied upon in bimetallic pairs, we do not recommend their use.

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Summary

1. Silicon carbide acts as an oxidation-reduction electrode, like platinum or other noble metal.
2. The results of earlier workers, which are at variance with ours, are to be attributed to a direct contact between solution and metallic conductor, and not to any property of the silicon carbide itself.

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