

Simard G L, Steger J F, Arnott R J & Siegel L A. Vanadium oxides as oxidation catalysts. *Ind. Eng. Chem.* 47:1424-30, 1955.
[Research Division, American Cyanamid Co., Stamford, CT]

Of the several vanadium oxides, only $V_2O_{4.34}$ and V_2O_5 are catalytically active in the production of phthalic anhydride from o-xylene. The surface is pictured as a dynamic surface involving changes from V_2O_5 -like to $V_2O_{4.34}$ -like structures. A result is that factors necessary for a good catalyst are inherently provided. [The SCI® indicates that this paper has been cited in over 95 publications since 1961.]

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"At the time the title work was done, I was assistant group leader in physical chemistry at the Stamford Laboratory of the American Cyanamid Company. The group leader, J.K. Dixon, had been interested for a long time in the action of vanadium oxide catalysts in oxidizing hydrocarbons. American Cyanamid then had a plant at Bridgeville, Pennsylvania, making phthalic anhydride from naphthalene. It was not difficult, therefore, to start a project on fundamental studies of this catalyst. Working with me were J.F. Steger conducting laboratory experiments, and L.A. Siegel and R.J. Arnott doing X-ray diffraction measurements. Their work contributed greatly to the success of the project.

"The oxidation of o-xylene was picked for convenience of operations. We ran so-called normal conditions and determined the phases of the catalyst along a fixed-bed tube. We investigated at the 'break-in' and conditions of overloading. The results showed that

a not too well-known oxide, $V_2O_{4.34}$, was active. In fact, V_2O_5 without added oxygen oxidized o-xylene to normal products and itself changed to $V_2O_{4.34}$.

"This led us to study the absorption of oxygen on the various vanadium oxides. V_2O_5 insufficiently oxidized, or to which a slight amount of V^{+4} was added, irreversibly adsorbed oxygen at 400° and 500°C, the temperature of reaction. The uptake of oxygen was controlled by the V^{+4} ions in an otherwise changing arrangement of V_2O_5 and $V_2O_{4.34}$. To show the structural change, a movie with models was actually made. Proof was that oxygen can be easily added or taken away under the conditions of reactions.

"Accompanying the travel of oxygen was the need for electron transfer. Accordingly, we then looked at the electrical conductivity characteristics of the oxides. As a function of temperature, V_2O_5 showed semiconductive behavior throughout, while $V_2O_{4.34}$ above 100°C changed to metallic behavior. Adding 0.5 percent V^{+4} to V_2O_5 likewise changed its behavior partly to metallic conduction. It was evident that electrons were present and readily available to participate in surface reactions.

"The picture we drew of the catalytic action of V_2O_5 was a dynamic surface of V^{+4} , V^{+5} , and O^{2-} ions in continually varied and changing structures. An ample supply of defect centers and low energy electrons are available for the reaction. Factors necessary for a good catalyst are inherently provided.

"The work was continued by H. Clark and D.J. Berets¹ after I left American Cyanamid, and summarized by J.K. Dixon and J.E. Longfield.²

"The reason the work was cited frequently was probably that it was basic work on a catalyst of commercial interest. As for all basic studies, the results have lasting interest."

1. Clark H & Berets D J. Vanadium oxides as oxidation catalysts: electrical properties. (Farkas A, ed.) *Proceedings of the International Congress on Catalysis*, Philadelphia, Pennsylvania, 1956. New York: Academic Press, 1957. p. 204-14.
2. Dixon J K & Longfield J E. Hydrocarbon oxidation. (Emmett P H, ed.) *Catalysis. Volume VII. Oxidation, hydration, dehydration and cracking catalysts*. New York: Reinhold, 1960. p. 183-280.