[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, ILLINOIS INSTITUTE OF TECHNOLOGY]

# Vanadium Oxides, Hydrogenation Catalysts. II[1]

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In the catalytic hydrogenation of unsaturated hydrocarbons on metallic or metallic oxide surfaces there is much evidence for the assumption that the chemisorption of the hydrocarbon is an important factor. In a recent paper, Twigg and Rideal[3] demonstrated that ethylene could be adsorbed on nickel atoms spaced at their distance of closest packing in the crystal surfaces, 2.47 Å.

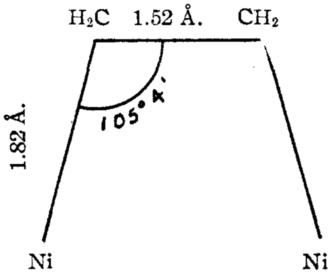

Fig. 1.—Nickel–ethylene complex.

Taking the distances C–Ni = 1.82 Å., C–C = 1.52 Å. (Fig. 1), the angle subtended was found to be 105°4′ in lieu of the tetrahedral angle of 109° 28′. Thus only a small distortion of the valence angle is necessary to effect the ethylene–nickel complex formation. The nickel atoms would have to be spaced a distance 2.73 Å. apart to avoid any distortion. This explains briefly the spatial conditions necessary for chemisorption of olefinic hydrocarbons.

TABLE I

SPACINGS AND RELATIVE INTENSITIES OF THE VANADIUM TRIOXIDE POWDER PATTERN OBSERVED IN SAMPLES OF VANADIUM PENTOXIDE REDUCED AT VARIOUS TEMPERATURES

s = 1.00, m = 0.6–0.8, w = 0.3–0.5, vw = 0.1–0.3, vvw = 0.02–0.1 (barely visible)

| $V_2O_3$ ASTM Card no. 3655 | | $V_2O_5$ red. at 425° | | $V_2O_5$ red at 400° | | $V_2O_5$ red. at 375° | |
|---|---|---|---|---|---|---|---|
| 3.65 | 0.6 | 3.66 | wm | 3.62 | vw | | |
| 2.70 | .8 | 2.71 | m | 2.71 | w | 2.71 | vvw |
| 2.47 | .6 | 2.48 | wm | 2.49 | w | 2.48 | vvw |
| 2.32 | .02 | | | | | | |
| 2.18 | .2 | 2.18 | w | 2.18 | vw | 2.18 | vvw |
| 2.03 | .02 | 2.04 | vvw | | | | |
| 1.83 | .25 | 1.83 | w+ | 1.82 | vw | | |
| 1.69 | 1.00 | 1.69 | s | 1.69 | m− | 1.69 | w |
| 1.61 | 0.02 | 1.64 | vvw | | | | |
| 1.57 | .03 | 1.57 | vvw | | | | |
| 1.470 | .25 | 1.470 | w | 1.466 | vw | | |
| 1.235 | .04 | | | | | | |
| 1.218 | .02 | 1.218 | vvw | 1.218 | vvw | | |
| 1.193 | .02 | 1.196 | vvw | 1.190 | vvw | | |
| 1.170 | .06 | 1.170 | vvw | 1.170 | vvw | | |
| 1.125 | .03 | 1.121 | vvw | 1.124 | vvw | | |
| 1.093 | .06 | 1.092 | vvw | 1.090 | vvw | | |
| 1.057 | .06 | 1.057 | vvw | 1.055 | vvw | | |

In a recent paper[1] the catalytic activity of a coprecipitated vanadium oxide–aluminum oxide catalyst (35% $V_2O_5$, 65% $Al_2O_3$) was reported for the hydrogenation of isobutylene at 300, 325, 350, 375 and 400°. The activity was excellent at 400°, but fell off rapidly as the reaction temperature was decreased from 400°. It was therefore of interest to investigate the spatial arrangement of vanadium oxides. Catalyst samples reduced at 300, 325, 350, 375, 400 and 425° were subjected to X-ray diffraction analysis in an attempt to find an explanation for the variation of the catalyst activity with temperature.

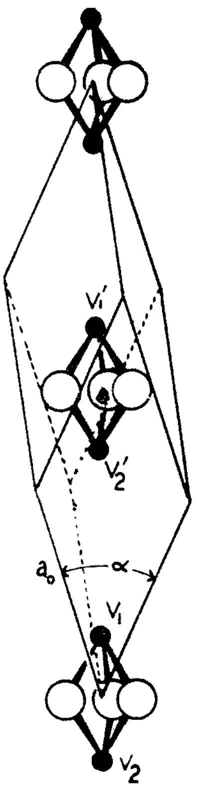

Fig. 2.—Unit cell of $V_2O_3$: $a$ = 5.45 Å., $\alpha$ = 53°49′, $v_1 - v_2$ = 2.78 Å., $v_1 - v_2'$ = 4.16 Å. Small circles represent vanadium atoms; large circles represent oxygen atoms.

The catalyst pellets were powdered and the material mounted in thin-walled pyrex capillaries 0.5 mm. in diameter. Powder patterns were obtained using CuK$\alpha$ radiation with General Electric diffraction equipment. The exposure time was four hours for each sample. Spacings were measured and relative intensities estimated visually, using a General Electric Illuminator. The intensities and spacings of the powder patterns obtained from the samples reduced at 425, 400 and 375°, along with the pattern of $V_2O_3$ recorded in the ASTM card file are presented in Table I.

It is evident that the amount of vanadium trioxide increases rapidly as the temperature of reduction approaches 400°. Samples reduced at 350° and below gave crystal powder diffractions, but the patterns indicate the absence of any vanadium trioxide. A weak pattern of aluminum oxide appeared on all the films. The fact that the reaction temperature giving maximum activity coincides closely with the temperature at which the pentoxide is reduced to the trioxide indicates that the trioxide is the active catalyst.

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(1) For Paper I of this series, see Komarewsky, Bos and Coley, THIS JOURNAL, **70**, 428 (1948).

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(3) Twigg and Rideal, *Trans. Faraday Soc.*, **36**, 533 (1940).

The spatial characteristics of vanadium trioxide will now be considered. The structure of vanadium trioxide has been shown to be based[4] on the hexagonal space group $D_3{}^6d$. The unit cell, as shown in Fig. 2, is a rhombohedron with $a = 54.5$ Å., $\alpha = 53°49'$, and contains two molecules of vanadium trioxide. On this basis, the vanadium atoms lie on the three-fold axis of the unit rhombohedron. The distance between vanadium atoms in the vanadium trioxide molecule is 2.78 Å. The closest distance of approach of vanadium atoms in the neighboring molecules is 2.98 Å. Figure 3 is a projection of the vanadium atoms on the rhombohedral $(01\bar{1})$ plane.

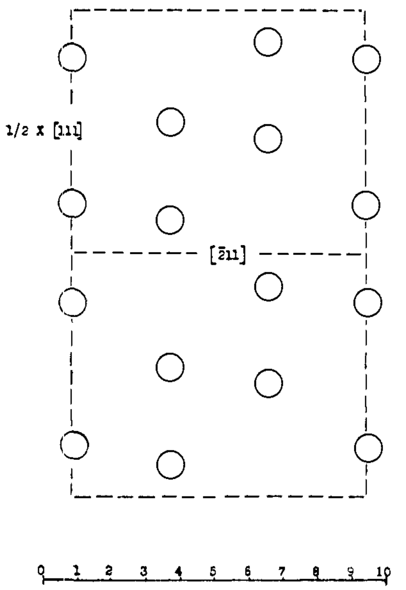

Fig. 3.—Projection of the vanadium lattice in $V_2O_3$. The plane of projection is $[01\bar{1}]$.

The angle subtended was found to be 108° 4′ as opposed to the tetrahedral angle of 109° 28′. Thus the formation of the vanadium–ethylene complex as shown in Fig. 4 may be effected with very little distortion and it may be estimated that vanadium trioxide will be a highly active hydrogenation catalyst.

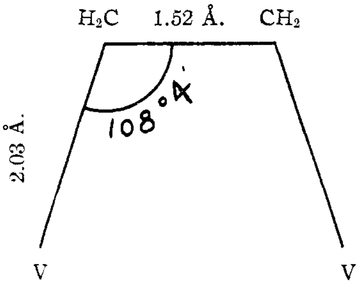

Fig. 4.—Vanadium–ethylene complex.

In the course of this work possible spatial relations between the ethylene molecule and the vanadium lattice in the vanadium pentoxide crystal structure were also examined. The formation of the vanadium–ethylene complex necessitated a greater distortion of the valence angle than for vanadium oxide.

It is highly probable that in many cases where vanadium oxide is reported as a hydrogenation or dehydrogenation catalyst, the active component is vanadium oxide, provided, of course, the reaction temperature is in the neighborhood of 400°.

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## Summary

1. The formation of the vanadium–olefin complex in the chemisorption of olefins on vanadium oxide may be effected with very little distortion of the valence angle.

2. The reaction temperature at which vanadium oxide gives maximum activity as a hydrogenation catalyst corresponds closely with the reduction temperature of vanadium pentoxide to vanadium oxide.

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[4] Zachariasen, *Skrifter Norske Videnskaps—Akad. Oslo I. Mat.—Naturv. Klasse*, No. 4 (1928).