α-aluminium oxide catalyst caused the total surface area to be increased, from that of the bare support which has a surface area of 3·5 m²/g⁻¹.

For example, (1) surface area of sample with 6·2 per cent nickel = 7·0 m²/g⁻¹ (nickel present as nickel oxide); (2) surface area of sample with 7·2 per cent uranium = 1·0 m²/g⁻¹ (uranium present as uranium oxide (U_3O_8)); (3) surface area of sample with 5·65 per cent total metal oxide = 12·0 m²/g⁻¹ (that is, nickel = 2·7 per cent + uranium = 2·95 per cent).

Because uranium (as U_3O_8) on α-aluminium oxide gives rise to very small surface area values—the highest recorded is 5·0 m²/g⁻¹—it is apparent that the uranium is either: (a) reducing the crystallite size of the nickel atoms; or (b) combining with the nickel to form a compound of high total surface area.

A preliminary X-ray examination of these catalysts has shown the existence of a new phase, probably as a result of the combination of nickel and uranium. From the X-ray data so far available, it is thought, however, that a situation exists where both of the foregoing alternatives occur simultaneously.

When a catalyst is prepared which contains this complex a much stronger adsorption of hydrogen is observed, when compared with catalysts containing nickel alone. These observations were made by obtaining differential thermal analysis thermograms on the fully reduced catalysts.

The presence of uranium in these catalysts also has important effects on the kinetics of the reactions involved in the steam–hydrocarbon reforming reactions. For example, for the butane (C_4H_{10})–steam reaction at 30 atm. pressure and 450° C, the reaction is described by

$$\frac{d\,(C_4H_{10})}{dt} = \frac{k(C_4H_1)_0{}^{0\cdot6}}{(H_2O)^{0\cdot6}}$$

while the corresponding kinetic expression for a nickel catalyst is

$$\frac{d\,(C_4H_{10})}{dt} = k\,(C_4H_{10})^0(H_2O)^1$$

From the foregoing kinetic expressions it is seen that water is more strongly adsorbed on the nickel/uranium catalyst than on a catalyst containing nickel alone. It is thought that this stronger adsorption of water will help to inhibit "coke" formation, which is an important limiting factor in the operation of these catalysts.

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New Identifications in the Oxygen Second Negative System

THE oxygen second negative band system is a result of the transition $A\,^2\Pi_u - X\,^2\Pi_g$. It is a system of red-degraded double-headed bands, extending from 1900 Å to 6500 Å, and the separation of the heads of each band is 200 cm⁻¹. The bands were first observed by Johnson[1] and further identifications have been made by other workers[2-6]. A list of band-head wavelengths, taken from refs. 1–5,

has been published by Wallace[7]. The frequencies of the band heads are given by

$$\nu_{v'v''} = \,^{38596}_{38796} + [898\cdot9(v' + \tfrac{1}{2}) - 13\cdot7(v' + \tfrac{1}{2})^2] - [1876\cdot4(v'' + \tfrac{1}{2}) - 16\cdot53(v'' + \tfrac{1}{2})^2] \quad (1)$$

This communication reports the observation of several bands that have not been reported previously and the re-assignment of vibrational quantum numbers and wavelengths for a few known bands. The system was excited in a liquid oxygen cooled discharge through oxygen (pressure = 0·005 torr) and helium (1·0 torr) at a current of 20 m.amp. The spectrum was photographed for 3 min using a Hilger large quartz prism spectrograph. The reciprocal dispersion was about 3 Å/mm at 2700 Å and 10 Å/mm at 4000 Å. The experiment was designed to measure integrated intensities, so a wide slit (80μ) was used, reducing the accuracy of the wavelength measurements to ± 0·5 Å. The helium lines appearing on the spectrogram were used as standards.

The new bands and those for which new assignments have been made are listed in Table 1. The suffixes i and ii in the v'' column refer to the shorter and longer wavelength head of the band. The letter in the last column refers to the comments below.

Table 1. NEW ASSIGNMENTS FOR SOME $O_2{}^+$ SECOND NEGATIVE BANDS

λ	ν (Observed)	ν (Calculated)	v'	v''	
2703·2	36982	36987	3	2ii	b
2705·3	36954	36961	5	3i	b
2806·1	35626	35627	8	5i	b
2821·0	35438	35427	8	5ii	a
2962·0	33751	33749	1	3i	c
2980·0	33547	33549	1	3ii	a
3141·0	31828	31827	5	6i	b
3143·0	31808	31804	1	4ii	b
3127·9	31961	31954	3	5i	c
3148·1	31756	31754	3	5ii	c
3277·2	30505	30492	8	8ii	a
4219·1	23695	23695	3	10ii	d
2548·1	39233	39212	11	4i	e
5736·1	17429				e
6433·0	15541	15510	0	14i	e
6531·8	15305	15310	0	14ii	e

(a) New bands. (b) Both the bands 3, 2ii and 5, 3i had previously been assigned the same wavelengths, but I have observed that they are clearly separated[8]. The 1, 4ii band had previously been assigned the wavelength 3141·0 Å. The band measured at 3143·0 Å in the present experiment corresponds more closely in wavelength and intensity with the assignment 1, 4ii. The much weaker band at 3141·0 Å has been given the assignment 5, 6i. (c) All these bands were originally measured by Lal[4] on a small quartz spectrograph; the present measurements give better agreement with the calculated values. (d) This band was measured by Johnson[1], who did not assign any quantum numbers to it. (e) These bands were all measured by Byrne[6], but his assignments gave very poor agreement with equation 1. The present assignments fit into the general scheme and are also reasonable as regards intensity. No reasonable assignment could be found for the band at 5736·1 Å.

A complete and up to date list of all the band head wavelengths for the system has recently been prepared together with a photograph showing all the new bands[8].

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[1] Johnson, R. C., Proc. Roy. Soc., 105, 683 (1924).
[2] Ellsworth, V. M., and Hopfield, J. J., Phys. Rev., 29, 79 (1927).
[3] Mulliken, R. S., and Stevens, D. S., Phys. Rev., 44, 720 (1933).
[4] Lal, L., Phys. Rev., 73, 255 (1948).
[5] Feast, M. W., Proc. Phys. Soc., A, 63, 557 (1950).
[6] Byrne, J., Proc. Phys. Soc., A, 78, 1074 (1961).
[7] Wallace, L., Astrophys. J. Suppl., 7, 165 (1962).
[8] Linton, C., Ph.D. thesis, London (1966).