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# The preparation of tungsten oxide powders with high specific surface areas

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Tungsten oxide powders with high specific surface areas ($50\,m^2g^{-1}$) are prepared by using a variation on the hot kerosene drying technique. It is also shown that the use of a water in oil emulsion in the hot kerosene drying technique has no effect on the specific surface areas of the resultant powders. The reason for the absence of any effect is explained. The difference between the powders prepared by the hot kerosene drying technique and the variation of this, is the high specific surface area due to the porous structure of the powders prepared by the latter method.

## 1. Introduction

The hot kerosene drying (HKD) technique to form finely divided inorganic powders was first described by Reynen *et al.* [1]. In the technique a solution containing one or more metal salts is first dispersed in kerosene together with an emulsifier to form a stable water in oil (w/o) emulsion. This emulsion is then added dropwise to a kerosene bath, thermostated at approximately 200° C. Upon addition of the emulsion to the hot kerosene the water evaporates and a finely divided salt is produced. A metal oxide powder can then be obtained by calcination of the salt above the decomposition temperature.

This technique was used by Lemaitre *et al.* [2] to produce lithium- and vanadium-doped iron oxides with specific surface areas of as much as $23\,m^2\,g^{-1}$. From this result it seems that the HKD technique could be useful in producing metal oxide powders with high specific surface areas for use as catalysts. However, no literature could be found on the effects of the different experimental parameters (e.g. degree of dispersion of the water phase, metal salt concentration, etc.) on the specific surface area of the resulting metaloxide.

It is the aim of this paper to point out that, at least for tungsten oxide powders produced from ammonium(meta)tungstate (amt), the specific surface areas do not depend on the dispersion of the water-phase in the w/o emulsion. The specific surface areas of the tungsten oxide powders prepared by the HKD technique are relatively small and an alternative method is given to prepare powders with specific surface areas ten times larger.

## 2. Experimental procedure

### 2.1. Preparation of samples

Finely divided tungsten oxide powders were prepared using the HKD technique and two variations. In the HKD technique a w/o emulsion of the amt solution in kerosene (ratio 1:1) was added dropwise ($4\,ml\,min^{-1}$) to a kerosene batch thermostated at 200° C. The emulsion was made by dispersing a solution of amt ($(NH_4)_6H_2W_{12}O_{40}$, Fluka pract., $12.5\,g\,dm^{-3}$) in kerosene (Exsol D, Esso chemicals) containing 4 vol % emulsion stabilizer (Span 80, ICI) using a special mixer (EMU Voss of Maldon). The drying apparatus was so designed that the evaporated water condensed in its upper part and was continuously removed. The metal salts produced were washed in acetone and dried overnight at 100° C. The oxides were obtained by calcination of the salts in air for 1 h at different temperatures.

Variation I. No emulsion was made and the amt solution was added directly to the hot kerosene, under the same conditions as in the HKD technique. The resulting metal salts were treated in the same way as above.

Variation II. The same procedure as for the HKD technique except that an o/w emulsion was used. The emulsion was stabilized by 8 vol % Tween 80 (ICI). Upon addition of the emulsion to the kerosene bath, partial decomposition of the Tween 80 emulsifier takes place. This yields a tar-like product in which the metal salt particles are contained. However, calcination at 400° C for 1 h burns off most of the organic material and tungsten oxide is obtained.

It was established with X-ray diffraction that in all cases well crystallized tungsten trioxide was obtained after calcination of the metal salt at 400° C or higher, for 1 h.

### 2.2. Thermal stability of w/o emulsions

The thermal stability of the w/o emulsion was investigated.

After preparation, 100 ml batches of the emulsion were placed in different water baths thermostated

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TABLE I Typical specific surface areas obtained with the different drying methods

| Method* | Specific surface area† ($m^2\,g^{-1}$) |
|---|---|
| HKD technique | 3.8 |
| Variation I | 4.2 |
| Variation II | 50.9 |

*Ammonium (meta) tungstate concentration in all cases 12.5 g $dm^{-3}$.
†After calcination at 400° C for 1 h in flowing air.

TABLE II The effect of the ammonium (meta) tungstate concentration on the specific surface area of the resultant tungsten-oxide powders, using variation I

| Concentration ($g\,dm^{-3}$) | Specific surface area* ($m^2\,g^{-1}$) |
|---|---|
| 25.0 | 2.9 |
| 12.5 | 4.7 |
| 6.3 | 3.2 |
| 3.1 | 4.0 |

*Powders washed in acetone and dried at 100° C for 16 h.

at 40, 60 and 80° C, respectively. After 1 and 3 h a sample was taken from each emulsion and cooled in another water bath to 25° C. No measurable sedimentation had taken place after 3 h for any of the batches.

A micrograph of the sample was taken at × 1000 using an oil immersion lens. For this a Zeiss light microscope equipped with a Leica camera was used. A micrograph of the emulsion immediately after preparation was also taken.

## 2.3. X-ray diffraction analysis

X-ray powder analysis was carried out in a standard Philips X-ray diffractometer using the Cu$K\alpha$ radiation.

## 2.4. Scanning electron microscopy

The samples were mounted with an epoxy on standard copper discs and carbon coated, to make them conductive. The SEM studies were done with a Cameca Canebax Microsonde.

## 2.5. Pore size distribution and surface area measurements

Nitrogen adsorption isotherms were determined by using the equipment and method similar to that described by Lippens *et al.* [3]. From the nitrogen adsorption isotherms the pore surface area distribution [4] and BET surface areas ($A$) were calculated. Total pore volumes ($V_p$) were taken at a relative pressure of 0.95 and the average pore radius ($\bar{r}_p$) was taken as $2V_p/A$.

# 3. Results

## 3.1. Sample preparation

Table I presents typical specific surface areas obtained with the different drying methods. Comparison of the specific surface areas of the tungsten oxide powders obtained by the HKD technique and by variation I shows that the presence of a w/o emulsion has no advantage in creating a larger specific surface area.

The effect of the amt concentration on the specific surface areas was investigated using variation I. From Table II it can be seen that varying the amt concentration between 25.0 and 3.0 g $dm^{-3}$ does not have any effect on the specific surface areas of the powders formed.

The specific surface area of 50.9 $m^2\,g^{-1}$ obtained with the o/w emulsion (variation II, Table I) was unexpected. Fig. 1a shows the effect of the calcination temperature and Fig. 1b the effect of the calcination time on the specific surface area of the tungsten oxide prepared in this way.

The development of the pore structure as a function of calcination time at 400° C was followed by nitrogen adsorption isotherms and pore area distributions (Figs 2a and b). Changes in the specific surface area, pore volume and average pore radius are summarized in Table III. It may be noted that very little hysteresis is observed after 1 h calcination. This points to the existence of tubular-type capillaries, closed at one end [5]. A mixture of A and B type hysteresis develops after calcination for 4 and 6 h, indicating the formation of a mixture of ink-bottle type pores and capillaries with slightly widened bodies [5].

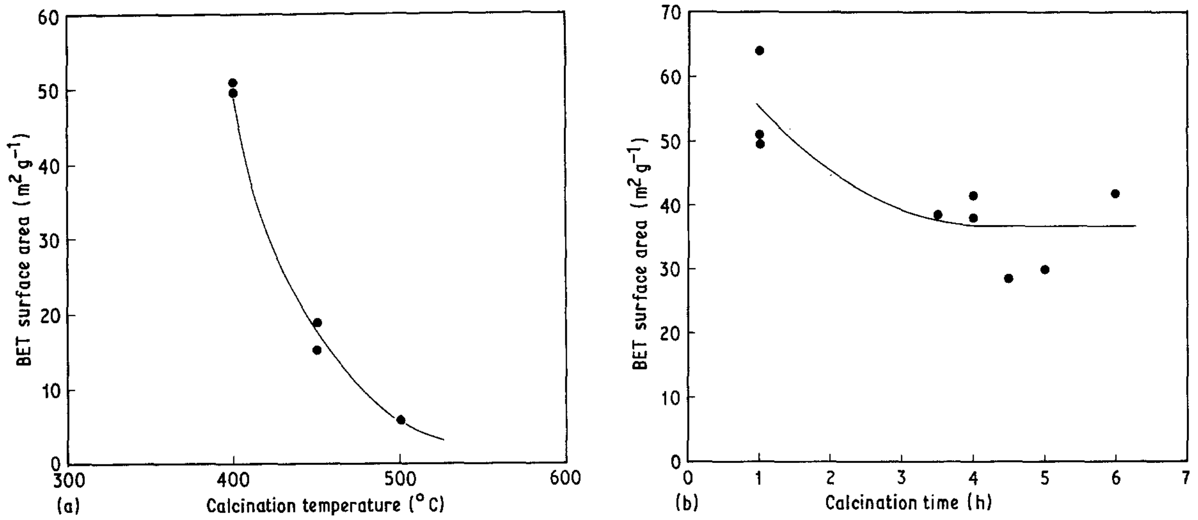

*Figure 1* BET surface areas of tungsten oxide powders prepared with variation II as a function of (a) calcination temperature (time 1 h), and (b) calcination time (temperature 400° C).

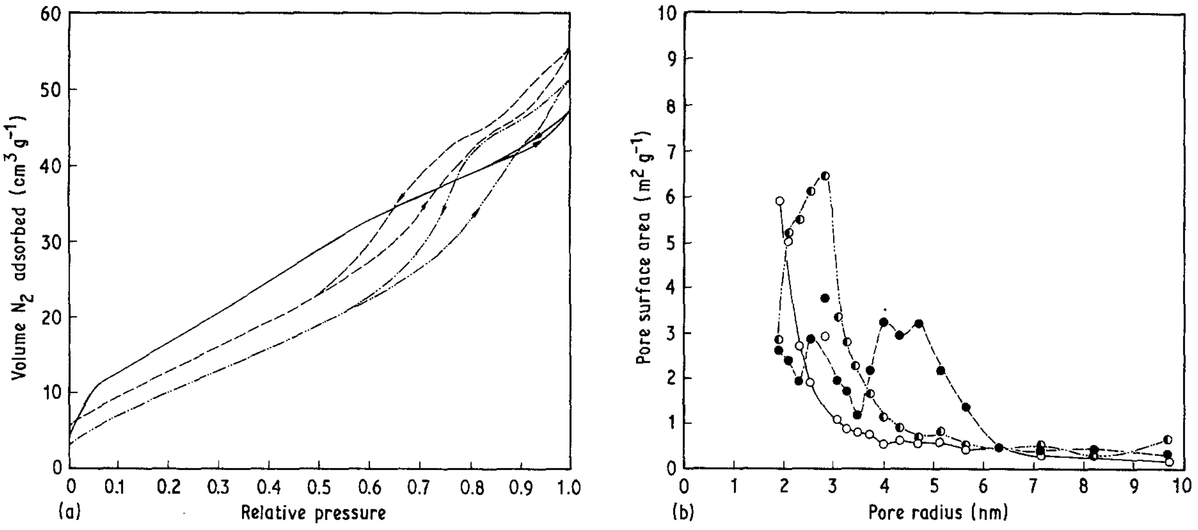

*Figure 2* (a) Nitrogen adsorption isotherms and (b) pore area distributions of tungsten oxide powders prepared with variation II and calcined at 400° C for different lengths of time: (○) 1 h, (◐) 4 h, (●) 6 h.

The specific surface area decreases after 4 h calcination and the average pore diameter nearly doubles. These two parameters remain constant after 6 h calcination. The total pore volume remains constant with increasing calcination time.

The high specific surface area observed for this powder can be expected to be due to an effect of the emulsifier that was used. In an o/w emulsion, the amt solution forms the matrix and a similar result to that obtained by variation I is expected. To investigate the influence of the Tween 80 emulsifier, different percentages (vol/vol) were added to a 12.5 g $dm^{-3}$ amt solution. This was then added to the hot kerosene. Fig. 3 presents the effect of the Tween 80 concentration on the specific surface areas of the resultant tungsten oxide powders, after calcination for 1 h at 400° C. From Fig. 3 it is clear that the Tween 80 has a significant effect on the specific surface area.

## 3.2. Thermal stability of w/o emulsions

The photograph taken of the emulsion immediately after preparation shows that the amt-solution droplets are of similar dimensions to the resolution of the microscope, i.e. approximately 0.5 μm. The emulsion is very homogeneous and no breakup is visible. However, as the emulsion is heated up the water droplets start to fuse to form droplets as large as 10 μm after 1 h at 80° C. After 3 h at 80° C droplets as large as 20 μm have formed. These results clearly show that the emulsion is unstable at higher temperatures. It can be expected that fusion of the water droplets will also take place during the heating up period upon addition of the emulsion to the hot kerosene bath.

TABLE III Parameters calculated from the nitrogen adsorption isotherms of tungsten oxide powders after calcination at 400° C for different lengths of time

| Calcination time (h) | Specific surface area ($m^2 g^{-1}$) | Pore volume ($cm^3 g^{-1}$) | Average pore radius (nm) |
|---|---|---|---|
| 1.0 | 64.0 | 0.069 | 2.1 |
| 4.0 | 41.5 | 0.078 | 3.9 |
| 6.0 | 41.8 | 0.073 | 3.5 |

## 3.3. Scanning electron microscopy

Fig. 4 presents typical SEM pictures of tungsten oxide powders prepared by variations I and II. The powders prepared by variation I consist of mainly spherical particles with a diameter of ~ 1 μm. Assuming an average specific surface area of 3.7 $m^2 g^{-1}$ and solid spherical particles, an average particle diameter of 0.22 μm was calculated. This correlates well with the 1 μm obtained from the SEM pictures, especially if some surface roughness is taken into account.

The tungsten oxide prepared by method I consists of relatively large porous particles (10 to 50 μm) with irregular shapes.

Fig. 5 presents SEM pictures of tungsten oxide powders prepared with different concentrations of Tween 80, 0.5% and 1.0%. The surface texture of the tungsten oxide in these two powders is clearly different. The surface of the tungsten oxide produced using 0.5% Tween 80 consists of partially sintered particles, some of which are smaller than 0.1 μm. However, if 1% Tween 80 is used the resulting

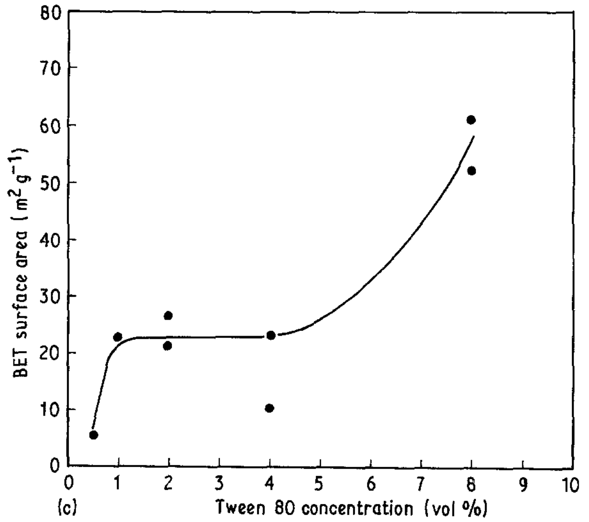

*Figure 3* BET surface areas of tungsten oxide powders prepared by variation II as a function of Tween 80 concentration (powders calcined for 1 h at 400° C).

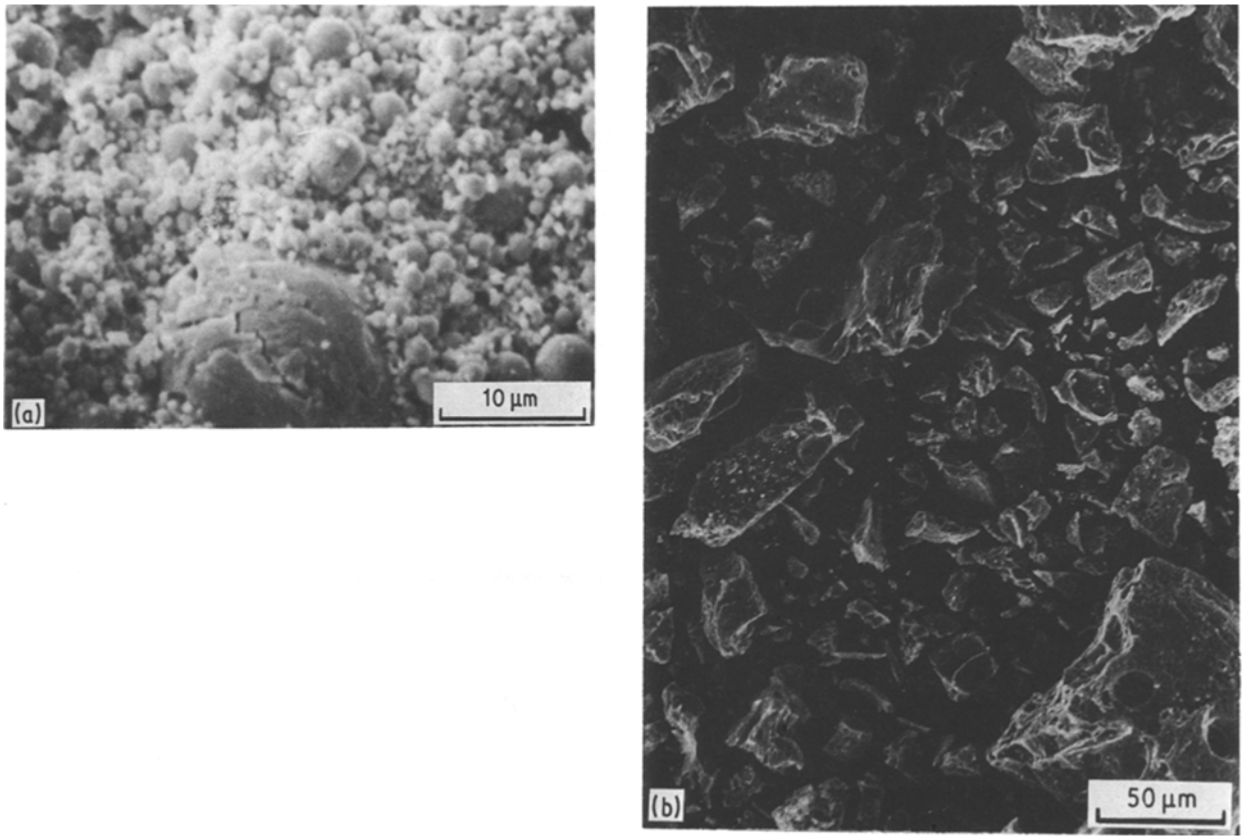

*Figure 4* Scanning electron micrographs of tungsten oxide powders prepared by variation I(a) and II(b). (Calcined for 1 h at 400° C.)

tungsten oxide is more porous and the surface itself is smoother. Partially sintered small particles are no longer clearly visible.

## 4. Discussion

The direct addition of an amt solution (3.1 to 25.0 g dm$^{-3}$) to the hot kerosene bath yields a tungsten oxide powder with the same specific surface area as that obtained by the HKD technique. Consequently, is there no advantage in starting with w/o emulsion. The powders prepared with the HKD technique and variation I consist mainly of spherical tungsten oxide particles that have a diameter of $\sim 0.5$ to 3.0 $\mu$m and a specific surface area of around 4 m$^2$ g$^{-1}$. The calculated external surface area of smooth spherical particles with a diameter of 0.5 $\mu$m is 1.7 m$^2$ g$^{-1}$. This value is close to the measured value and the difference can be explained in terms of surface roughness which is not accounted for in the calculated value. From the above comparison it is clear that the tungsten oxide particles must be largely non-porous.

The results from the thermal stability experiments with the w/o emulsion give a good indication why the HKD technique fails to produce higher specific surface area powders than obtained with variation I. Each amt solution droplet with a diameter of 0.5 $\mu$m contains enough amt to produce a spherical tungsten trioxide particle with a diameter of 0.1 $\mu$m. Particles with this diameter have a calculated specific surface area of 8.4 m$^2$ g$^{-1}$.

The fact that the measured particle diameter is larger and the specific surface area smaller means that fusion of the amt solution droplets must take place before the water phase has evaporated. This is in accordance with the observed instability of the emulsion at temperatures above 40° C.

From the above results it follows that the emulsion breaks up during the time it heats up after addition to the hot kerosene and before the water phase has evaporated completely. This explains why the dispersion of the water phase in kerosene to form an emulsion before addition to the hot kerosene bath has no advantage over a direct addition of the amt solution.

The tungsten oxide produced by variation II differs considerably from that produced by the HKD technique and variation I. The high specific surface area of this powder is due to its porosity as is evident from the scanning electron micrographs (Fig. 4b) and the nitrogen adsorption isotherms (Fig. 2a). Initially (1 h calcination) the pores are mainly tubular-type capillaries as is indicated by the absence of any significant hysteresis in the absorption isotherm [5] (Fig. 2a). Longer calcination times cause a 35% loss in specific surface area and nearly a doubling of the average pore radius, but no significant change in the pore volume (Table I). The increase in average pore radii is also visible in the pore area distributions (Fig. 2b). The development of a type A/type B hysteresis indicates a change in pore structure. The new pores are a mixture of the ink-bottle type and of capillaries with widened bodies. Putting the above results together it appears that longer calcination times causes some capillaries to fuse together. This creates larger pores and a loss in specific surface area, as observed. This process should have no influence on the total pore volume which is also in accordance with the observations.

Addition of Tween 80 to the amt solution results in

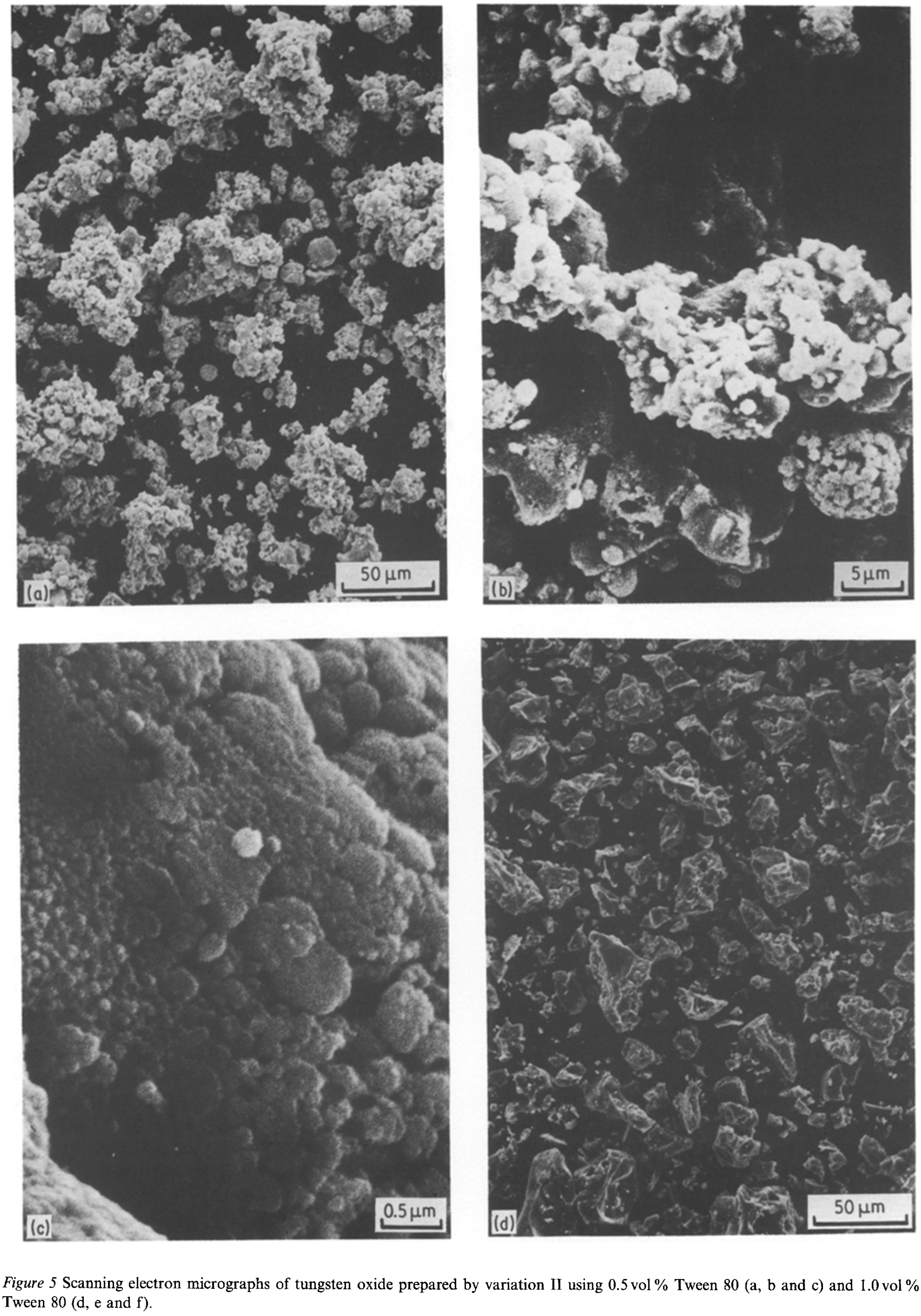

*Figure 5* Scanning electron micrographs of tungsten oxide prepared by variation II using 0.5 vol % Tween 80 (a, b and c) and 1.0 vol % Tween 80 (d, e and f).

a considerable increase in the specific surface area of the tungsten oxide powder. To explain the effect of Tween 80, different concentrations were added to the amt solution. As can be seen in Fig. 3, there is an increase of approximately 500% in the specific surface area upon addition of 1 vol % Tween 80 and a further doubling when 8 vol % is added. By comparing the electron micrographs of the powders prepared by 0, 0.5 and 1.0 vol % Tween 80 (Figs 4a, 5a to c and Figs 5d to f, respectively) a clear change in the physical

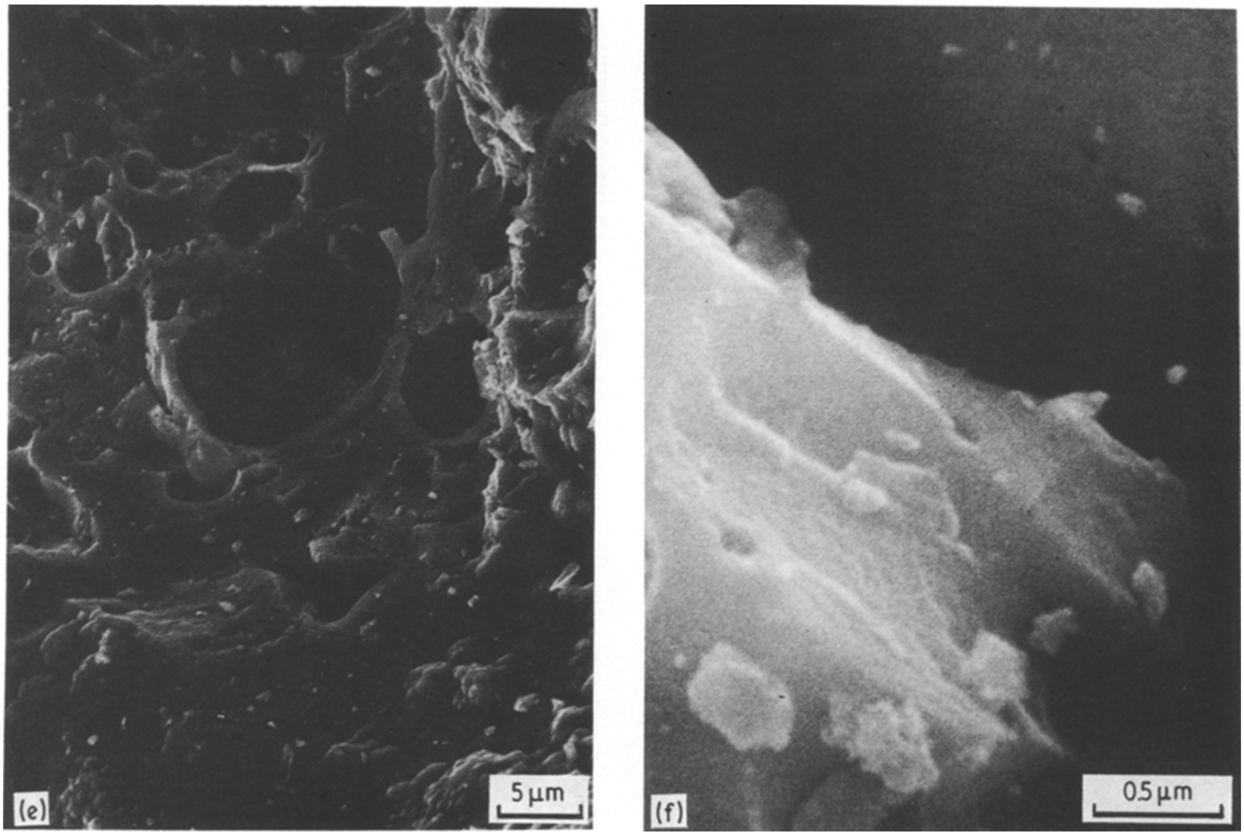

*Figure 5* Continued

structure of the particles can be seen. Addition of 0.5 vol % Tween 80 results in large porous particles (Fig. 5a), but further enlargements (Figs 5b and c) show that these consist of partially fused smaller particles. These small particles have diameters ranging from 1.0 to > 0.1 μm. Addition of 1.0 vol % Tween 80 (Fig. 5d) results in tungsten oxide particles very similar in appearance to those obtained with 8 vol % Tween 80 (Fig. 4b). However, in Fig. 5e some remains of partially fused particles between 2 and 1 μm can still be seen.

Based on these results the following hypothesis to explain the formation of a porous tungsten oxide upon addition of Tween 80 to the amt solution, is proposed. Tween 80 is a poly-oxi-ethylene-(20)-sorbitan-mono-oleate and this compound has, due to the large polar group it contains, a low solubility in kerosene. Upon addition of the amt solution to the kerosene the water starts to evaporate and the amt solution becomes more concentrated. The moment that the amt concentration reaches a certain level crystallization starts. In this process a heterogeneous surface is created on which the Tween 80 then adsorbs and by doing so inhibits further crystal growth. The driving force for the adsorption is the heterogeneity of the surface and the rapid increase in the Tween 80 concentration as the water evaporates. The low solubility of the Tween 80 in kerosene prevents it from dissolving into the kerosene. The resulting product is a Tween 80 matrix containing amt particles $\ll 0.1$ μm.

Upon calcination the Tween 80 matrix is partially boiled off and partially burned away. At the same time the small amt crystallites start decomposing and sintering. In this way a porous tungsten oxide powder is produced. A Tween 80 concentration of 0.5 vol % is insufficient to completely inhibit the growth of amt crystallites. Consequently, on average larger amt particles are formed which do not readily sinter at 400° C and have a lower specific surface area.

The following points can be mentioned as evidence for the above process.

1. Partial decomposition of Tween 80 is observed, but when an 8 vol % Tween 80 in water solution is added to the hot kerosene bath in the absence of amt, no decomposition takes place. The decomposition of Tween 80 can be explained in terms of its adsorption on the amt-crystallites. The heterogeneous surface of the crystallites then serves as a catalyst for the Tween 80 decomposition.

2. The X-ray diffraction pattern of the amt crystallites in the Tween 80 matrix shows broad poorly defined reflections. This indicates that the amt is either poorly crystallized or that the crystallites are very small $\sim 3$ nm.

3. After calcination at 400° C for 1 h tungsten oxide particles smaller than 0.1 μm are still visible (Fig. 5c). This means that particles of this size are resistant to sintering at 400° C and this implies that the amt particles obtained with 1 vol % Tween 80 must be smaller. However, amt tends to form particles of approximately 0.5 μm in the absence of Tween 80. Particles significantly smaller than this can only be produced when the growth process is inhibited.

In this process Tween 80 acts as a surfactant and by doing so suppresses or inhibits crystal growth. We expect that the extent of suppression is a function of the size of the polar group in the surfactant. Using surfactants with smaller or larger polar groups, could lead to effective tailoring of the primary metal salt particles. This, in turn, gives control over the specific surface areas of the resultant powders. Ideally the surfactant should not decompose during adsorption under reaction conditions.

## 5. Conclusion

Tungsten trioxide powders can be prepared using the HKD technique. However, starting with a w/o emulsion is not a prerequisite, as the direct addition of the water solution produces a powder of similar structure and specific surface area.

The specific surface area of this powder is low and an alternative technique is described to prepare a tungsten trioxide powder with a specific surface area of a factor of ten higher.

The physical structure of this high surface area powder is different in that the particles are porous and irregularly shaped. There are indications that these high specific surface areas are a result of suppressed primary particle growth of the metal salt during preparation and consequent sintering during calcination.

The idea is also advanced that surfactants with different polarities which do not degrade under preparation conditions could be used to tailor the primary particle size. In this way the specific surface area of the resultant metal oxide powders could be controlled.

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