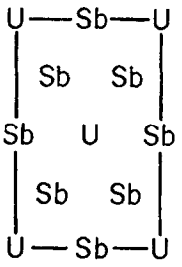
TABLE 2
INTERATOMIC DISTANCES (Å) FOR PHASE I—USb_3O_{10}

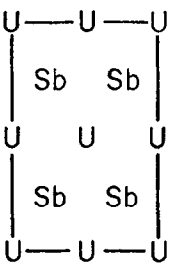
$U–O_I$ (4) = 2.44	$Sb_I–O_I$ (4) = 2.04	$Sb_{II}–O_I$ (2) = 1.93
$U–O_{III}$ (2) = 1.80	$Sb_I–O_{II}$ (2) = 1.85	$Sb_{II}–O_{II}$ (1) = 1.88
$U–O_{IV}$ (2) = 2.54		$Sb_{II}–O_{III}$ (1) = 2.17
		$Sb_{II}–O_{IV}$ (2) = 1.95
$(U–O)_{av}$ = 2.31	$(Sb_I–O)_{av}$ = 1.98	$(Sb_{II}–O)_{av}$ = 1.97

closely related. This can be shown in the following way, considering heavy atoms only:



USb_3O_{10}

(at z = 0.000)
Phase I



$USbO_5$

(at z = 0.000)
Phase II

Actually, the structures are pseudo-hexagonal, related to α-UO_3, as has been found by Kovba and co-workers (*7*) in some other mixed uranium oxide systems.

TABLE 3
UNIT CELL FOR PHASE II
Formula $USbO_5$; system, orthorhombic.

a = 7.53 Å
b = 13.04
c = 15.80
Z = 16
ρ_{obs} = 7.74 g/cc, ρ_{calc} = 7.53

In all cases the superstructure is orthorhombic.

More complete discussion of the above including additional physical data will be reported shortly.

REFERENCES

1. GRASSELLI, R. K., AND CALLAHAN, J. L., *J. Catal.* **14**, 93 (1969).
2. (*a*) BOOMAN, G. L., MAECK, W. J., ELLIOT, M. C., AND REIN, J. E., *Anal. Chem.* **31**, 1130 (1959); (b) ELKIN, A., GAYER, K. H., AND BOLTZ, D. F., *Anal. Chem.* **25**, 1744 (1953).
3. CHEVALIER, M., AND GASPERIN, M., *C. R. Acad. Sci. Ser. C* **267**, 481 (1968).
4. WELLS, A. F., "Structural Inorganic Chemistry," 3rd ed., p. 675 ff and 965 ff. Oxford Univ. Press, London/New York, 1962.
5. CHEVALIER, M., AND GASPERIN, M., *C. R. Acad. Sci. Ser. C* **268**, 1426 (1969).
6. EFREMOVA, O. A., KOVBA, L. M., AND SPITSYN, V. I., *Zh. Strukt. Khim.* **10**, 344 (1969).
7. KOVBA, L. M., SIROTKINA, E. I., AND TRUNOV, V. K., *Zh. Neorg. Khim.* **10**, 349 (1965).

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Controlled Impregnations Via Displacement of an Immiscible Liquid

The initial step in the preparation of a supported catalyst is the impregnation of the support with a solution of the desired metal salt. As ordinarily carried out in the laboratory, impregnations are rather ill-defined. Thus, the repetitive sequence of

adding a dose of solution to the support, and then hand-mulling, is virtually impossible to describe in detail and no two individuals are likely to perform an impregnation is precisely the same manner. The problem of inhomogeneity in the finished impregnate definitely exists, especially in the preparation of larger batches where the hand-mulling becomes laborious. In view of the fact that automated procedures are taking over so many aspects of experimental catalysis, the present technique of support-impregnation must be judged to be somewhat archaic.

We have developed a technique for impregnation with aqueous solutions which eliminates the laborious hand-mulling and reduces the details of the impregnation to a few easily-controllable parameters. We have chosen the title, "Displacement-Of-Immiscible-Liquid," because the method involves slurrying the support with a water-immiscible liquid in a high-speed mixer, e.g., Waring Blender or Osterizer, and adding the (aqueous) impregnating solution from a buret. As the common oxide supports are more hydrophilic than oleophilic, the aqueous solution displaces the water-immiscible liquid from the pores of the support, and the latter is thereby impregnated.

When the desired volume has been added from the buret, agitation is interrupted and the mixture is filtered. The filtrate is observed to be clear and water-white, i.e., pure hydrocarbon which can be reused. The filter-cake is broken up with a spatula to facilitate evaporation of occluded hydrocarbon and the resulting solid has the look and feel of a well-impregnated catalyst. If the impregnating solution is colored, the impregnate will have uniform color intensity.

The three parameters needed to describe an impregnation by the displacement method are: (1) the slurry parameter, ml/g, i.e., the volume of hydrocarbon used to slurry a given quantity of support; (2) the dosage, ml/g, of aqueous solution added to impregnate a given quantity of support; and (3) the rate, ml/min, at which solution is added from the buret. The fact that all three parameters are easily controlled is conducive to reproducible impregnations.

Ordinary laboratory stirrers cannot be used for displacement impregnations. If water and hydrocarbon are stirred with one, stopping the agitation leads to immediate separation into two phases. Quite different results are achieved with a Waring Blender (10000 rpm or higher). Agitation, even for a few seconds, of a small amount of water in hydrocarbon results in a dispersion stable at least 15 min after stirring has been stopped. The water droplets will range from submicron to about 10-μ size. The displacement method is thus characterized by a very gradual contacting of support with the impregnating solution. This contrasts with manual impregnation, in which a small area of support is contacted by a great excess of liquid poured onto it. This locally-drenched condition must be alleviated (probably never completely) by hand-mulling.

We have found that 400 ml of heptane in a 1-qt Waring Blender will slurry 40–50 g of typical supports such as Al_2O_3 or MgO. The dosage parameter must be determined by trial for each support, as in the case of manual impregnations. Compared with the latter, however, displacement-impregnation dosages are generally found to be lower by about one-third. This reflects hydrocarbon not displaced from the pores. If the correct dosage is exceeded in a displacement impregnation, the impregnate, after filtration and evaporation of hydrocarbon, will have a pasty consistency. The same, of course, is true if too much solution is used in a manual impregnation.

We have used rates of addition of aqueous solution in the range 2–8 ml/min. This does not seem to be a critical parameter and it is quite possible that still higher rates could be used.

The following practical suggestions should be noted:

1. Explosion-proof blenders, which are commercially available, should be used. This is due to the possibility of hydrocarbon leaking through the bearing and into the motor. If an ordinary blender is

used, a fire extinguisher should be handy in case of flashing.

2. It is advantageous to connect the end of the buret, via plastic tubing, to a hypodermic needle. The buret is then mounted so that the aqueous solution is discharged well below the liquid level in the blender.

3. Although almost all the impregnated support will pour freely from the blender (unless a large excess of solution has been added), some impregnated solid may adhere to the wall. If desired, this material can be recovered by scraping the walls and briefly re-blending.

In conclusion, we have used the displacement method with a large number of supports and have been pleased with the increased control, reproducibility, and freedom from manual effort which this method affords.

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