

The Preparation and Use of Ultrathin Metal Films as Model Systems for Highly Dispersed Supported Catalysts

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A technique is described for the preparation, under ultrahigh vacuum conditions, of ultrathin metal films for use as catalysts. These films have an *average* "thickness" of the order of a "monolayer" of metal on the substrate. It is suggested that film catalysts of this type may be used as models for highly dispersed technical metal catalysts. Their use is illustrated by the reactions of *n*-hexane on ultrathin platinum and nickel film catalysts.

INTRODUCTION

Highly dispersed supported metal catalysts are of great industrial importance. The degree of dispersion, that is the particle size of the metal, is important not only in controlling the surface area per unit weight of metal, but it is also clear that the nature of the catalytic process can be considerably modified by the particle size. As a typical example of the latter we may cite the work of Maat and Moscou (1) who showed that in the reaction of *n*-heptane over platinum/alumina catalysts, the proportion of dehydrocyclization products decreased and of isomerization products increased as the platinum particle size increased in the range 10–500 Å.

The degree of dispersion of some supported metal catalysts has been estimated by gas adsorption by Spenadel and Boudart (2) and by electron microscopy combined with a thin sectioning technique by Moss (3).

Although it is possible to exercise a degree of control over particle size in supported catalysts, there still remains a sizable gap between the use of this type of catalyst and surface studies which have been (and are currently being) carried out with the clean surfaces of bulk metals such as thick evaporated metal films, or metal single crystals. The difficulties of comparing

the surface chemistry in these two types of systems include the problem of surface cleanliness (i.e., knowing the actual state of the surface) of supported catalysts, as well as the problem of controlling and defining the nature of the metal particles.

It seemed to us that there was a need for a model system for supported catalysts where surface cleanliness and (hopefully) particle size and structure could be better controlled, and where the substrate upon which the metal particles were located could be well characterized, thus permitting epitaxial relations to be established. The purpose of this short article is to suggest that ultrathin metal films are useful for this purpose, and to describe a laboratory technique for their preparation and use. We also illustrate their use in some actual reactions, but we propose to leave a detailed description of their catalytic properties for a subsequent paper.

In the present sense, we take the term "ultrathin" to mean a film where the *average* surface concentration of metal atoms on the substrate is of the order of one monolayer (although the metal is probably present as very small crystals). We know of no previous studies using films of this type as catalysts; the nearest appears to be some work by Moss *et al.* (4) who prepared a range of evaporated silver

film catalysts down to a surface density of about $1 \mu\text{g cm}^{-2}$ (equivalent to an average surface concentration of silver atoms of about 5 monolayers). After having been deposited on glass at 0°C and used in a catalytic reaction at 120°C , a silver film of density $1 \mu\text{g cm}^{-2}$ had an average crystal diameter of about 120 Å. This relatively large crystal size is, at least in part, a reflection of the great ease of sintering of silver films. However, we note that no provision was made in this work for the elimination of silver deposited during filament outgassing, and it may be that the film structure was strongly influenced by the density of silver nuclei deposited during filament outgassing, and this was done under bakeout conditions with the glass substrate at 450°C . For adequate control over ultrafilm structure it is obviously very desirable to avoid depositing the working film on top of an "outgassing film," and the apparatus to be described has been designed with this end in view.

EXPERIMENTAL METHODS

All films were prepared under ultrahigh vacuum conditions, and we have used both platinum and nickel. Platinum was evaporated from a hairpin filament consisting of 0.3-mm diameter tungsten wire overwound with 0.1-mm diameter platinum wire (5). The tungsten was thoroughly cleaned down to bright metal before use. Preliminary cleaning and outgassing, including the evaporation of some platinum was done in a separate system. Outgassing, including some further evaporation, was continued after the filament was mounted in the reaction vessel. With a platinum-on-tungsten filament of this type the final outgassing after mounting in the reaction vessel is particularly protracted, but was continued until a pressure of about 1×10^{-9} Torr was achieved. Nickel was evaporated from a hairpin filament of 0.5-mm diameter nickel wire, and was subjected to a similar preliminary outgassing procedure. Johnson and Matthey Specpure grade materials were used. The pressures measured during film deposition fell within the range $1-10 \times 10^{-9}$ Torr: with the substrate

at $<100^\circ\text{C}$, the pressures were near the bottom of this range, while with the substrate at 275°C , the pressures were near the top end.

In order to use an ultrathin metal film as a reaction catalyst under controlled conditions, it is obvious that the reaction volume must contain no other exposed metal surface upon which the reaction can proceed. On the other hand, the small quantity of metal present in an ultrathin film places something of a premium upon vacuum conditions during film preparation, so that thorough outgassing of the evaporation source, including some preliminary evaporation, is essential. To meet these conflicting requirements, we have designed a reaction vessel which can be divided into two compartments by a lapped ground-glass sliding valve, and which is fitted with a movable evaporation source. This reaction vessel is shown in Fig. 1.

The movable evaporation filament F is spot-welded to the assembly A which is suspended by the electrical lead C. The lead C consists of three multistrand copper conductors, each encased in a thin woven silica ("Vidaflex") insulating sleeve, and in order to obtain the necessary flexibility, the individual wires in each multistrand conductor should not be greater than about 40 SWG. In normal operation, only two of the three conductors are needed to supply the filament, the remaining one only providing mechanical stability. In practice it is easy to provide leads of sufficient flexibility which can pass 15 A without appreciable heating. The copper wire must be compatible with UHV requirements, that is it must be clean, enamel free, and preferably OFHC. The woven silica sleeving should be degreased before use, since the fresh material may contain oil from the weaving process.

The lead C passes to the rotary windlass W via the radial guide D, and it finally terminates at the lead-throughs E. The weight M_1 (about 30 g) is necessary to tension the lead C and to make the filament assembly rise and fall vertically as the windlass is worked, and M_2 is a counterweight. The windlass is operated magnetically via the

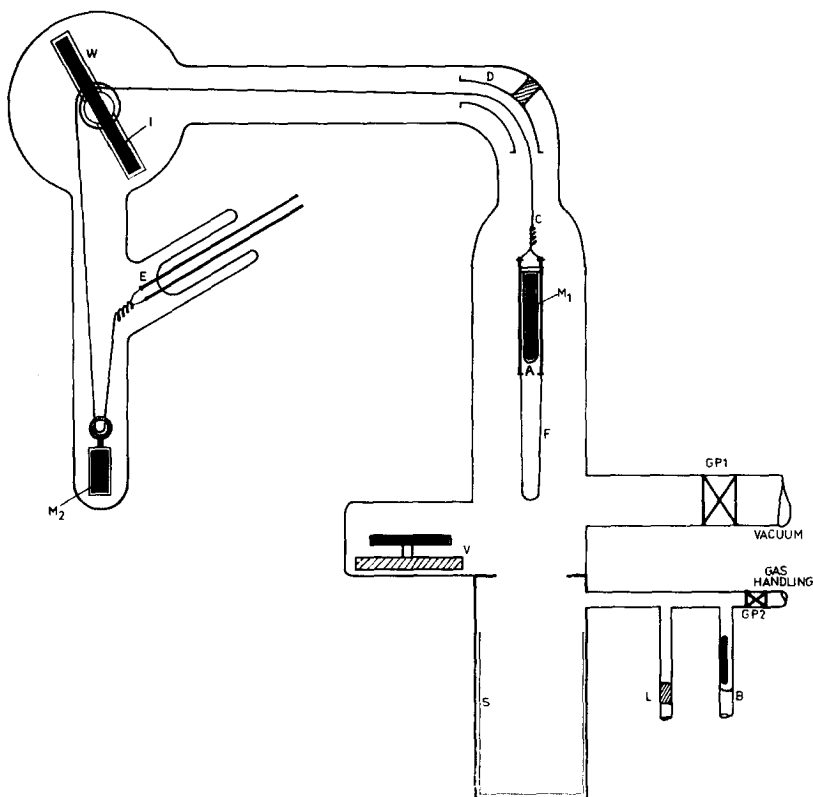


FIG. 1. Apparatus for the preparation and use of ultrathin metal film catalysts.

iron slug I which is adjacent to a flat end-window of the windlass case. The ground-glass isolation valve V is magnetically operated, and the iron slug on V as well as the iron slugs I, M₁, and M₂ are glass encapsulated. The positions of the Metrosil pellet leak and sample extraction break-seal are indicated at L and B, respectively. With the present design of apparatus, a pressure change during a reaction will result in the transfer of gas between the reaction volume and the rest of the apparatus across the isolation valve. This can result from a pressure change due to the reaction itself, from the removal of gas for analysis, or from temperature fluctuations. The effect of temperature fluctuations can easily be made negligible by adequate temperature control. The amount of gas removed via the mass spectrometer leak is usually very small, while the influence of a pressure change due to the reaction itself will be small if the reaction is limited to

the initial stages. The proportion of reactant removed for VPC analysis may well be substantial (typically $\leq 20\%$), and we have therefore generally adopted the procedure of terminating the reaction after the first VPC sample was removed, with the added precaution of estimating the extent of reaction from data for the reaction products rather than the reactant.

In use, the filament is hoisted into the upper compartment of the reaction vessel for outgassing and preliminary evaporation (with V closed), and the outgassed filament can then be lowered into the bottom portion of the vessel for deposition of the working ultrathin film and then withdrawn and the slider valve closed for a study of the reaction confined to the ultrathin film catalyst.

The films were deposited on a mica substrate which was of total area approximately 130 cm². The substrate and filament geometry were essentially the same as pre-

viously described (6) for use with normal thick films (cf. Fig. 1). From this geometry, and the visual appearance of thick (visible) films, it was estimated that the platinum in the ultrathin films was distributed over a substrate area of approximately 100 cm². The total quantity of metal in each film was determined by acid leaching from the substrate followed by analysis using for platinum the spectrophotometric method described by Payne (7), and for nickel atomic absorption spectrophotometry. The error in a metal estimation for a given film was about $\pm 5 \mu\text{g}$.

Specimens of ultrathin films for electron microscopy are readily prepared by peeling from that mica surface which carried the metal particles, an extremely thin mica flake which is thin enough to be transparent to electrons. The sensitivity for the detection of small metal crystals is limited mainly by the available contrast provided by the metal and the mica, and for this purpose, the thinner the mica, the better. However, with ultrathin films in the "monolayer" range, we have so far been unable to resolve any of the metal particles by electron microscopy. Nonetheless, we believe from experience with other metal films on mica, that with the present technique the presence of metal crystals 20–25 Å across would have been detected, and we therefore place this as a conservative upper limit to the particle size in these ultrathin films.*

An attempt has been made to provide an independent estimate of crystal size by measurement of hydrogen adsorption on an ultrathin platinum film (Shimoyama, unpublished data from this laboratory). It was found that the hydrogen uptake at 20°C was virtually independent of pressure in the range $4\text{--}10 \times 10^{-3}$ Torr, and this was taken to correspond to the formation of a monolayer of dissociatively chemisorbed hydrogen with a surface stoichiometry H/Pt of unity. A similar criterion has been

used with thick platinum films (8). With an ultrathin platinum film of 84 μg total weight and deposited on a substrate of 100°C, the hydrogen uptake was 1.4×10^{17} H₂ molecules. If spherical particles are assumed, with none of the surface platinum atoms sterically excluded from adsorption by the substrate, these data correspond to an average particle diameter of about 11 Å. It is most unlikely that reasonable alterations to the assumptions in the model could yield an average crystal diameter much in excess of about 15 Å. It should be noted that although the total amount of metal in the film is very small, the total surface area of platinum is substantial, being about 224 cm².

The measurement of total surface area of metal by (say) hydrogen adsorption illustrates that specific catalytic activity may be estimated using ultrathin film catalysts, provided the subsequent catalytic reaction is compatible with the prior adsorption.

EXAMPLES OF USE OF ULTRATHIN FILMS

As an example, we have studied the skeletal reactions of *n*-hexane (in the presence of excess hydrogen) on both platinum and nickel ultrathin films. The general design of the reaction system was the same as previously described (6). The composition of the reaction mixture was monitored via a Metrosil pellet leak to an MS10 mass spectrometer, while a break-seal could be used to extract reaction mixture for VPC analysis (cf. Fig. 1).

The initial reaction mixtures contained a hydrogen/*n*-hexane molar ratio of 10:1, and at the reaction temperature the total initial pressure in the reaction vessel was approximately 60 Torr. The reaction volume is estimated to contain initially about 3.6×10^{20} H₂ molecules and 3.6×10^{19} *n*-hexane molecules. The reaction volume is defined to be that isolated below the sliding ground-glass isolation valve (cf. Fig. 1). This isolation valve does not, of course, provide a vacuum-tight seal between the two regions in the apparatus. However, the following facts leave no doubt that the observed reaction is confined entirely to

* *Note added in proof:* This particle size has since been confirmed by direct electron microscopic observation which will be reported in a subsequent publication.

TABLE 1
SKELETAL REACTIONS OF *n*-HEXANE ON ULTRATHIN PLATINUM AND NICKEL FILMS^a

| Type of catalyst | Reaction temp (°C) | C ₆ reaction products (mole %) | | | | | | Selectivity | Total conversion (%) |
|--|--------------------|---|------|---------|-------|------|--------|------------------|----------------------|
| | | 2-MP | 3-MP | 2,3-DMB | neo-H | MCP | CH + B | | |
| Pt 1, 0.32 μg cm ⁻² , deposited 275°C | 273 | 10.5 | 4.5 | 0 | 0 | 73.7 | 11.3 | >10 ^b | 0.77 |
| Pt 2, 0.84 μg cm ⁻² , deposited 275°C | 273 | 12.5 | 5.6 | 0 | 0 | 72.4 | 9.5 | >10 ^b | 3.3 |
| Ni 1, 0.1 μg cm ⁻² , deposited 275°C | 273 | 11.6 | 26.6 | 0 | 0 | 0 | 61.8 | 0.12 | 0.6 |

^a 2-MP = 2-methylpentane; 3-MP = 3-methylpentane; 2,3-DMB = 2,3-dimethylbutane; neo-H = neo-hexane; MCP = methylcyclopentane; CH = cyclohexane; B = benzene.

^b Accuracy limited by uncertainty in methane estimation.

the ultrathin film catalyst. In the first place the rate of the reaction is certainly entirely negligible at any temperature less than, say, 150°C and care was taken to ensure that the film in the upper portion of the apparatus (the "outgassing film") was kept close to room temperature while the reaction occurred over the ultrathin film at 275°C. Secondly, blank reactions carried out in the absence of ultrathin film but in the presence of outgassing film showed absolutely no reaction products to be detectable. Thirdly, the ground-glass isolation valve had a rate constant for gas leakage in the molecular flow region of about 10% hr⁻¹ liter⁻¹, and with a valve of this magnitude, one would not expect reaction products to be detectable even if some reaction did occur on the outgassing film.

The reaction results are shown in Table 1. In Table 1, the selectivity is defined as the ratio of *n*-hexane molecules reacting to give C₆ products, to *n*-hexane molecules reacting to give C₁-C₅ products. Reaction over the ultrathin platinum films is noteworthy for both the very high value for the selectivity, and the large proportion of C₆ reaction products that appear as carbocyclics. This type of behavior is in agreement with the known properties of highly dispersed supported platinum catalysts. On

the other hand, with the ultrathin nickel catalyst the selectivity is low: most of the reaction proceeds by hydrogenolysis of the *n*-hexane, and methane was the largest single product by a considerable margin (about 70% of the total reaction products). This behavior of nickel relative to platinum is also in agreement with the known catalytic properties of these metals.

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