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DETERMINATION AND EFFECT OF PLATINUM CONCENTRATION PROFILES IN SUPPORTED CATALYSTS

By

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Abstract

Radial concentration profiles of platinum deposited upon cylindrical alumina pellets have been determined by means of electron-probe microanalysis. Specialized methods are described, whereby very low platinum concentration levels can be measured quantitatively under adverse specimen conditions. Profiles have been determined for catalysts containing uniform and non-uniform platinum distributions. Catalytic dehydrogenation data obtained on these catalysts indicate that a uniform platinum distribution can give higher activity.

Introduction

Supported catalysts prepared by the impregnation of a pre-formed support may contain the deposited constituent in a uniform or non-uniform distribution, depending on a variety of factors. An accurate determination of metal concentration profiles in supported catalysts has not, until recently, been possible. However, the technique of electron-probe microanalysis now provides a relatively general method for obtaining such data. The present investigation is concerned with the determination of platinum concentration profiles in platinum-alumina catalysts by electron-probe microanalysis, and a limited examination of the relationship between these measured profiles and catalytic dehydrogenation activity.

Platinum-alumina catalysts are frequently prepared by the impregnation of alumina particles with an aqueous solution of chloroplatinic acid, followed by drying and calcination of the impregnated composite. Such catalysts usually contain a non-uniform distribution of the platinum with most of the platinum being concentrated near the external surface of the catalyst particle. As such, they are sometimes described as "surface-activated" catalysts. This non-uniform distribution results from selective adsorption of the platinum constituent from the impregnating solution by the alumina

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support. A description of the phenomena involved in this selective adsorption has been proposed[1,2]. On the other hand, uniform distributions of platinum on alumina may be achieved by, for example, impregnation of the alumina with an ammoniacal aqueous solution of platinum diammino dinitrite, followed by drying and calcination. Thus, the platinum distribution can be controlled readily by choice of the method of catalyst preparation.

The scanning electron-probe microanalyzer[3,4] used to determine platinum concentration profiles is an instrument that can directly carry out elemental analyses of selected microregions, *in situ*, on the surface of a solid specimen. A high-voltage electron beam is focused to form a "probe" about 1 μ in diameter on the specimen, where it excites the characteristic X-radiation of the element(s) present. The resulting X-ray spectral data provide qualitative and quantitative elemental analyses of selected areas, lines, or points as small as one micron. Electron beam scanning, with synchronized oscilloscope displays, further provides direct portrayal of specimen surface-topography (back-scattered electron image), distribution of any selected element along a chosen line (linear concentration profile), or element distribution over an area (X-ray image)[5,6]. Although the electron-probe is uniquely suited for measuring the distribution of elements within individual catalyst pellets or granules, very little quantitative work of this type has been published.

In the present investigation, platinum concentration profiles have been determined for three different platinum-alumina catalysts, each of which had a total platinum concentration of 0.3% by wt as Pt. One of these had a relatively uniform platinum distribution, one had the platinum concentrated in a narrow layer at the surface, and the other had a distribution intermediate between these extremes. The catalytic activity of each of these catalysts was measured relative to the dehydrogenation of *n*-dodecane to linear dodecenes. This particular reaction has been studied previously in these laboratories[7,8] and served as a convenient model system for measuring dehydrogenation activity. It was ascertained that each of the three catalysts studied comprised a low acidity platinum-alumina composition, as discussed elsewhere[7]. They could, accordingly, be considered to be approximations of mono-functional catalysts possessing primarily a catalytic function associated with the platinum phase of the catalyst.

Experimental Methods

Electron-probe microanalyses. A Cambridge "Microscan, Mark II" electron-probe microanalyzer[9,10] was used. The cylindrical catalyst pellets were embedded in electrically-conductive graphite-loaded epoxy resin, sectioned

transversely through their approximate centers, ground flat, and aluminized.

Standard electron-probe procedures are usually based on metallo-graphic-type specimen mountings, with smoothly-polished plane surfaces. Because of the porous, granular texture of the alumina catalyst supports, however, the pellet sections have rough, irregular surfaces which may cause topographical "shadowing" effects, superimposed on the element distribution patterns displayed on X-ray images. Any gross differences in specimen-density within the image-area can also produce misleading effects, via corresponding localized variations in the intensity of emitted background X-radiation. Background X-ray image techniques were used to compensate for possible topographic and density effects, in the interpretation of the X-ray images.

The catalyst pellet mountings also fail to meet another necessary requirement for good electron-probe specimens, in that they have very low electrical conductivity. Even a relatively "heavy" vacuum-deposited aluminum film (about 500 Å thick) does not necessarily form a continuous conducting layer on the rough pellet surface, and as a result, the "specimen current" reading does not serve its normal function as a monitor of X-ray excitation level. This difficulty is circumvented by a method of interpretation based on peak/background ratios, as described later.

Three principal types of platinum distribution were encountered: (1) Pt distributed fairly uniformly throughout the pellets; (2) Pt only in the outer surface layer, about 300 μ deep; and (3) Pt mostly near the surface, but present at lower concentrations throughout the pellet.

On pellets with Pt throughout, a radial strip about 300 μ wide, extending from center to edge, was analyzed via a series of overlapping image fields. Scaler counts of Pt L_{a1} and background X-ray emission were recorded simultaneously with the photographing of the respective X-ray images, thereby obtaining "peak" and "background" X-ray intensities, which provide a quantitative measure of Pt concentration, field-by-field.

On samples having essentially all of the Pt present near the outer surfaces of the pellets, only edge-fields were studied, via electron, Pt L_{a1}, and background images, plus linear concentration profiles. The profile plots were photographed for about twelve repeated scans to average out the "noisy" statistical scatter inherent in low counting rates while retaining "minimum time-constant" response to sharp concentration gradients. For point-by-point excitation-level calibration, the background radiation profile was similarly photographed, at reduced oscilloscope brightness, and a zero-count baseline was traced by closing the X-ray slit for one scan.

On samples with Pt concentrated near the surface and also distributed at a lower concentration throughout the pellet, both the field-counts and concentration-profile procedures were used.

Catalyst preparations. Catalyst A was prepared by impregnation of $1/8 \times 1/8$ inch tablets of Harshaw activated alumina 0104 with an aqueous ammoniacal solution of platinum diammino dinitrite using the minimum solution technique, followed by drying of the impregnate at 120°C for 12 hr and calcination of the dried composite in air at a temperature of 500°C for 12 hr. Analysis of the final catalyst indicated a Pt content of 0.30% by wt. Catalyst B was prepared by impregnation of the same alumina used for Catalyst A with an aqueous solution of chloroplatinic acid using the minimum solution technique, followed by drying and calcination similar to that used for Catalyst A. Analysis indicated Catalyst B had a Pt content of 0.32% by wt. Catalyst C was obtained from Engelhard Industries, Inc. and consisted of $1/8 \times 1/8$ inch catalyst particles having a Pt content of 0.30% by wt.

The support used for Catalysts A and B had a surface area of 74 sq meters per gram and a sodium content of 0.20% by wt as Na. Catalyst C had a surface area of 84 sq meters per gram and a sodium content of 0.50% by wt as Na. The pore volumes of Catalysts A, B and C were similar, *i.e.*, 0.3 cc per gram.

Dehydrogenation activity. The reactor systems and analytical procedures used for obtaining data on *n*-dodecane dehydrogenation to linear dodecenes were the same as those described previously[8]. The reaction conditions employed in the present study were the same as those described elsewhere[7] for the platinum/alumina catalysts. Activity was determined from the results of a continuous run of 20 hr duration. During any given run catalyst deactivation occurs. For the present purposes, the dehydrogenation activity has been expressed as the average conversion of *n*-dodecane to linear dodecenes during the 20 hr run. It was established that the activity-time curve as well as average conversion to linear monoolefin was quite reproducible for a given catalyst.

Results and Interpretation

Micro-probe detection limits and accuracy. The various catalyst preparations contain platinum at average concentrations of 0.3% by wt. Local concentrations within pellets range from "zero" to several percent.

Under the conditions of these analyses, detection sensitivity and quantitative accuracy are not limited by available X-ray intensity or counting

statistics, but by instrumental factors, chiefly the long-term stability of the impinging electron-probe beam.

In initial exploratory work using relatively intense excitation (40 kv, about 1 μamp) Pt $L_{\alpha 1}$ emission of 550 c/s was obtained against 280 c/s background from 0.3 wt% Pt, *i.e.*, a peak/background ratio equivalent to 4.2/1 for 1% Pt. When peak and background X-rays are counted for three minutes each under these conditions, the detection limit imposed by counting statistics alone, *i.e.*, peak above background by three times the standard deviation of the background[4], is only 40 ppm. Our measurements have indicated that a true detection sensitivity of 100 ppm Pt in Al_2O_3 is attainable (*i.e.*, peak 3% over background) where high probe-intensity (*e.g.*, 40 kV, 1 μamp) can be used, so that about 50,000 counts are obtained in only a few minutes.

Probe intensities on this order, however, can only be used near a heat-sink, *i.e.*, on suitably embedded small catalyst particles or near the edges of larger pellet-sections. On whole-pellet mountings the 40 kV, 1 μamp beam fused and/or vaporized the pellet in a few minutes at distances $>200\ \mu$ from the mounting, even when the probe was continuously scanning a 400 μ square area.

For routine analyses, therefore, reduced beam intensities are necessary to prevent specimen deterioration. At 30 kV, 0.1 to 0.5 μamp, Pt $L_{\alpha 1}$ peak/background ratios for 1% Pt are about 3/1 via spectrometer scans and linear concentration profiles; about 2.2/1 via counting of entire imagefields. In the relatively fast routine analyses of the type examined for Catalyst B, it is estimated that the detection limit is about 300 ppm, and quantitative accuracy is $\pm 5\%$ of the amount present at concentrations above 0.5%; $\pm 10\%$ down to 0.2% Pt, and semi-quantitative down to the detection limit.

Peak/background ratios. In normal electron-probe analysis the incident beam intensity is adjusted to obtain and maintain a constant specimen-current reading, whereupon the characteristic X-ray peak intensity, with background subtracted out, closely approximates a linear measure of element concentration. High specimen resistivity drastically affects the specimen-current reading, however, so that the Pt $L_{\alpha 1}$ X-ray intensity observed at a given specimen-current is a function of local specimen-resistivity as well as Pt concentration. For example, to reproduce a given specimen-current for different catalyst samples, the required impinging-beam intensities varied as much as sixfold; and on a typical sample, specimen-current readings decreased threefold as the electron-probe was scanned several hundred microns inward from the pellet-section edge. Localized specimen-charging

effects introduce additional uncertainties as to the point-to-point constancy of the impinging beam.

Under these conditions, the best measure of Pt concentration is not the Pt $L_{\alpha 1}$ count-rate (over background), but the peak/background ratio (P/B). This ratio, with one background subtracted out ($P/B-1$) measures the Pt peak in terms of "background-levels". Thus the "white" background radiation level at a wavelength very near the characteristic Pt $L_{\alpha 1}$ line is used as the best measure of excitation level readily observable. This method compensates for topographical irregularities as well as resistivity variations. At low concentrations, background is an appreciable fraction of the peak intensity, so quantitative accuracy is not greatly sacrificed.

Sensitivity calibration. For the catalyst with fairly uniform distribution, the average Pt concentration in the radial strip analyzed was assumed equal to the known average weight percent Pt from chemical analysis of entire pellets. Pt $L_{\alpha 1}$ sensitivity was calibrated by simply equating the average emission (measured in terms of background levels, *i.e.*, $P/B-1$) to the known average percent Pt. The data were then plotted field-by-field to show percent Pt as a function of radial distance on the pellet. Where necessary, edge-field data were adjusted to allow for the portion of the field not occupied by the pellet.

For pellets having Pt concentrated near the surface, the following procedure was used to calibrated P/B ratios observed on the linear concentration profiles, in terms of true weight percent Pt, considering the geometry of the pellet.

The cylindrical pellet is considered as "n" concentric cylindrical shells of uniform thickness. The incremental volume V_i of shell "i" is expressed as its fraction of total pellet volume so that $\sum V_i = \text{unity}$. Insofar as the linear concentration profile represents the Pt distribution inward from any point on the pellet surface, the average Pt $L_{\alpha 1}$ intensity ($P/B-1$) over a small interval on the profile represents the average Pt concentration in the wall-volume of the cylindrical shell of corresponding thickness and depth. The total quantity "Q" of Pt in the pellet is represented by:

$$Q = \sum_{i=1}^{i=n} (P/B-1)_i \, V_i$$

with Pt concentration expressed in the arbitrary units of "background levels" of Pt $L_{\alpha 1}$ radiation (above the one level of true background). This value corresponds to the overall average Pt concentration, C_{avg}, which is known from chemical analysis of entire pellets. A Pt $L_{\alpha 1}$ intensity of "Q" (background-levels) therefore corresponds to a Pt concentration of "C_{avg}"

weight percent Pt, and a Pt $L_{\alpha 1}$ intensity of one background level (*i.e.*, a P/B ratio of 2/1) represents a local concentration, in weight percent Pt, C_{avg}/Q.

With this sensitivity-calibration factor, a vertical scale can be assigned to the linear concentration profiles, to read vertical oscilloscope deflection directly in terms of weight percent Pt plotted against distance on the specimen.

One linear concentration profile was checked against a line-by-line spectrometer-scan analysis. Each point plotted from spectrometer-scan data represented the average Pt content over a line about 300 μ long parallel to the edge. This plot was found to be in close agreement with the electronically-scanned profile of a single line perpendicular to the edge, indicating that the much faster concentration-profile procedure provides truly representative, quantitative information.

Calculation of platinum distribution. The weight-fraction of total platinum which is contained in a particular shell "j" is:

$$Fj = (P/B-1)jVj/Q$$

and the concentration in shell "j" is:

$$Cj\,(\text{wt}\%\ \text{Pt}) = (P/B-1)j \times C_{avg}/Q$$

The Pt distribution can be quickly calculated and expressed in terms of proportion and local concentration, for subsequent correlation with catalyst activity data; *e.g.*, for Catalyst B:

42% of the total Pt is present as ~0.8 wt% concentration in the outer 100 μ thick surface layer, which constitutes 17% of the total pellet volume;

27% of the total Pt is present as ~0.6 wt% in the next 100 μ layer (100–200 μ below the surface), which is 15% of pellet volume;

13% of the Pt is present as ~0.3 wt% in the next 100 μ layer (200–300 μ below the surface), 13% of pellet volume; and

18% of the total Pt is present as ~0.1 wt% in the remaining interior, 55% of total pellet volume.

For this calculation, the "shells" need not be of equal thickness, but can be chosen to fit the gradients observed on the linear concentration profile. The platinum concentration profiles determined by the concentration-profile procedure described above are given in Figure 1 for Catalysts A, B and C.

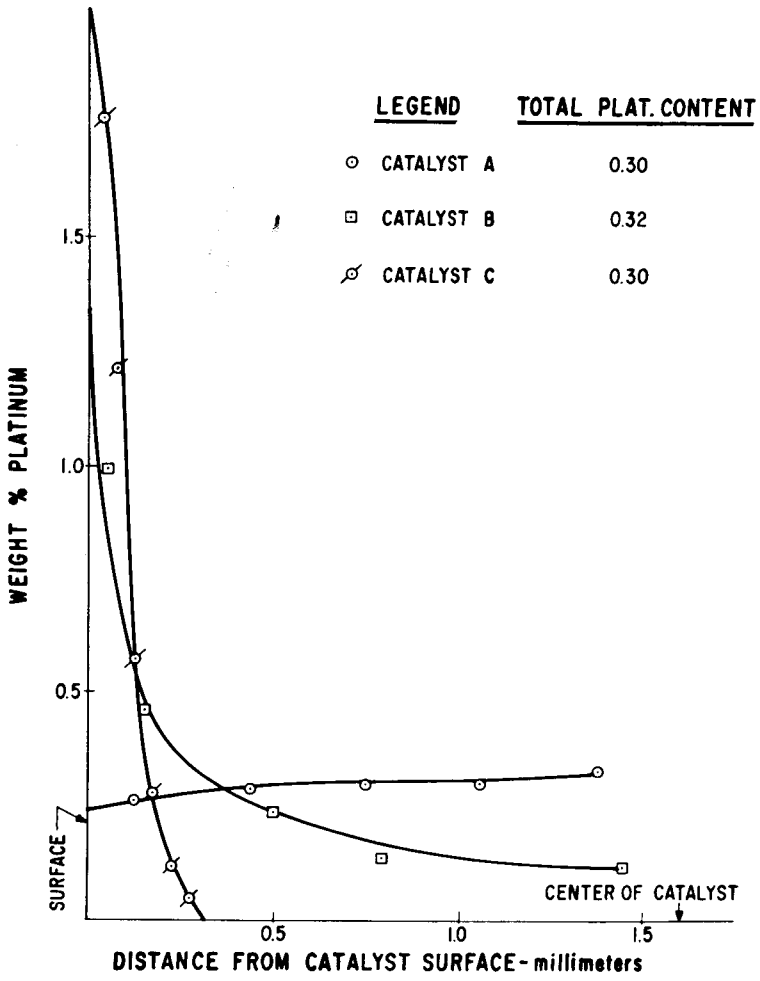

Fig. 1. Platinum concentration profiles.

Correlation of profiles with dehydrogenation activity. The results obtained on comparative dehydrogenation activity for the three catalysts are given in Table 1.

Catalyst *A* which has a nearly uniform platinum distribution has a higher activity than Catalyst *B* which is deposited on the same support with a non-uniform distribution. Catalyst *C* which is most acutely concentrated near the surface has the lowest activity of all. Although *C* is on a different support, the pore properties of the support are similar to those of the support used to prepare Catalysts *A* and *B*. Thus there is at

TABLE 1. Dehydrogenation activity at standard conditions

Catalyst	% Conversion to Mono-olefin*)
A	11.1
B	10.1
C	6.9

*) Average conversion over 20hr run.

least a qualitative trend indicating that the highest activity was obtained with a uniform distribution of platinum.

It was ascertained that all three of these catalysts exhibited low acidity,[7] that is, all three gave very low levels ($<1.0\%$) of skeletal isomerization and cracking in the dehydrogenation products. Thus these catalysts could be considered an approximation to mono-functional catalysts in which the dehydrogenation activity is derived principally from the platinum phase and would be sensitive to the state of the platinum. Catalyst *B*, prepared from chloroplatinic acid, was found to contain 0.3% Cl, but apparently this level of chloride was insufficient to impart appreciable strong acidity to the catalyst.

While the present data indicate that activity increased with increasing uniformity of platinum distribution, the origin of this result is difficult to infer from the concentration profile data alone. Other factors which could play a role include the relationship between local platinum concentration and activity, the state of platinum dispersion in each sample, the extent of intraparticle diffusional control of activity during the conditions used to measure activity, and possible variations in the distribution of platinum among pores of different sizes in each of the samples. Obviously, much additional data would be needed to isolate the role of each of these factors and to establish interacting effects. The present work has demonstrated that electron-probe microanalysis can be used to measure concentration profiles in supported catalysts and indicates that with the particular catalyst preparations studied there is an apparent correlation between activity and concentration profiles. While not examined in these studies, platinum concentration profile may also influence other catalytic properties such as resistance to sintering and stability upon regeneration.

The work of MAATMAN[2] indicates that at a given level of platinum concentration there are, among catalysts having a relatively uniform distribution of platinum, wide variations in activity. Some catalysts are more active and others less active than the one (no competitive adsorbate) with

a non-uniform distribution. The variations in activity reported by MAATMAN are very much greater than those observed in the present work, and suggest that when competitive adsorbates are used in the preparation of platinum catalysts, factors other than variations in the radial concentration profile must be exerting a profound influence, *e.g.*, chemical and physical effects arising from the influence of the competitive adsorbates.

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