JOURNAL OF CATALYSIS 63, 425–432 (1980)

Preparation of Nonuniformly Active Catalysts

YEN-SHIN SHYR AND WILLIAM R. ERNST[1]

School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332

Received September 27, 1979

The effect of adding chemical coingredients to H_2PtCl_6 impregnating solutions in order to modify Pt profiles in spherical γ-alumina beads was studied. Coingredients included the following acids and salts: HCl, HF, HNO_3, acetic acid, citric acid, tartaric, $AlCl_3$ NaCl, NaF, NaBr, $NaNO_3$, Na_3PO_4, Na benzoate, and Na citrate. Radial Pt profiles were examined by electron probe microanalysis of bead cross sections. Nine distinctly different types of profiles were produced. NaBr was the only coingredient which produced a monotonically increasing Pt profile from bead center to surface. A simple model which describes the role of NaBr during the impregnation process was discussed. A method of producing monotonically decreasing Pt profiles from bead center to surface which involves incorporating both NaBr and citric acid in H_2PtCl_6 impregnating solution was studied.

INTRODUCTION

Nonuniformity of activity in supported metal catalysts can occur as a result of catalyst preparation methods or catalyst poisoning. Nonuniformly active catalysts may in some processes exhibit superior activity, selectivity, or resistance to poisoning compared to uniformly active catalysts. Many recent papers have discussed theories of diffusion and reaction in nonuniformly active catalysts (*1*–*6*). Less attention has been focused on fundamental experimental studies which involve preparation, characterization, and evaluation of performance in kinetic studies involving probe reactions. Several challenging questions arise when one attempts such fundamental studies; e.g., what parameters should be adjusted during catalyst preparation in order to produce a desired distribution of active ingredient within a support particle? Quantitative measurement of mass distribution of active ingredient within a particle can easily be determined for metals by electron probe microanalysis, but how does one quantitatively measure "activity" distribution within a particle? Is it valid to assume constant diffusivity throughout a nonuniformly active catalyst particle, as often assumed in published models? Experimental verification of model predictions is necessary if one is to have confidence in these models as tools for design.

A recent paper presented the theoretical basis for a kinetic study to determine the effect of activity distribution in spherical catalyst particles on selectivity of the deuterium–hydride exchange reaction (*7*). The catalyst considered was alumina-supported platinum. (This reaction was shown previously to be a suitable probe for diffusional influences in uniformly active catalysts (*8*, *9*)). This paper presents results of the catalyst preparation phase of this study. A later article will report results of characterization and kinetic studies.

Impregnation was selected as the means of preparing the catalysts because of its simplicity and wide use. Previous workers have developed ways of producing uniform profiles of active ingredient (e.g., (*10*, *11*)) and sharply defined profiles such as outer shells, inner shells, and cores (e.g., (*12*–*14*)). Workers have investigated many preparation variables and their influence on the distribution of active ingredient in a number

---

[1] To whom all corresondence should be addressed.

0021-9517/80/060425-08$02.00/0

of metal–support combinations (*11*, *15–18*). There exists a broad body of knowledge of the physical and chemical processes of the impregnation process and surface chemistry of support materials (e.g., (*19–28*)). However, each metal–support combination is unique and hence introduces new challenges to the investigator.

An objective of this work was to investigate the possibility of using chemical additives (coingredients) in impregnating solutions as a means of controlling the distribution of active ingredient within the catalyst particle. Platinum on spherical γ-alumina beads was the system studied. Of particular interest for our future kinetic studies would be the ability to approximately reproduce some of the profiles that are considered in theoretical studies previously mentioned (*3–6*)—e.g., profiles which monotonically increase or decrease from particle center to surface. Linearly increasing or decreasing profiles were frequently considered in these theoretical studies.

Catalysts which have monotonically decreasing profiles are of some interest in kinetic studies because they serve as models of partially poisoned catalysts. There may also be commercial interest in such catalysts especially for reactions which are diffusion limited and in which the catalyst undergoes a shell progressive poisoning. They may exhibit activity or poisoning resistance that is superior to uniform or shell profiles.

Hexachloroplatinic acid was the active ingredient selected for this study. The strong interaction between H_2PtCl_6 and γ-alumina is known to produce shell catalysts which have a well-defined boundary between Pt and bare support. Citric acid was employed as an additive to the H_2PtCl_6 solution because this combination is known to produce core catalysts. The approach that was used to find a means of controlling Pt profile was: first, to explore the interactions of H_2PtCl_6 and citric acid with the alumina supports; second, to experimentally survey a large number of chemical additives which, when included in the impregnating solutions, modify the shell or core profile; and third, to select and further investigate the chemical additive which yields the Pt profiles desired.

EXPERIMENTAL METHODS

A 0.0564 *M* stock solution of H_2PtCl_6 was prepared by dissolving Fisher Certified $H_2PtCl_6 \cdot 6H_2O$ in deionized and carbon-treated water. Solution concentrations were determined by a spectrophotometric method (*29*) on a Bausch and Lomb spectrophotometer. Concentrations were expressed as moles of Pt per liter. A 0.1 *M* stock solution of citric acid (CA) was prepared from Fisher Certified CA. Solution concentrations were determined by titration. Stock solutions of various acids or salts (Table 1) were prepared to give concentrations of about 0.1 *M*. γ-Alumina beads of spherical geometry (Rhône Poulenc Inc., GOD-30) had the following properties: diameter, 0.36 cm; bulk density, 0.3 g/cm^3; surface area, 150 m^2/g; total pore volume, 1.70 cm^3/g; and average pore diameter, 450 Å.

Adsorption isotherm experiments involved contacting eight alumina beads (ca. 0.1 g) with 0.5 cm^3 of solution containing CA or H_2PtCl_6 at 25°C. All solutions were prepared by diluting the stock solutions described above. After 2 hr of contacting, beads were separated from solution by filtration and washed with 2 cm^3 of water to quantitatively remove and recover external solution. Washing time and volume were kept to a minimum to avoid removal of active ingredient from pore solution. The recovered solution was diluted with water to a volume of 5 cm^3 and analyzed for active ingredient. The amount of adsorption was determined by the difference between initial and final concentrations of active ingredient in solution after correcting for pore volume.

In experiments designed to test a large number of acids and salts as coimpregnating ingredients, solutions were prepared by adding stock solutions of H_2PtCl_6, acid or salt solution, and water in the volumetric ratio 1 : 1 : 8. The experimental procedure involved placing eight alumina beads in contact with 0.5 cm^3 of impregnating solution for 1 or 22 hr at 25°C. The beads were removed from solution, washed with 2 cm^3 of water, dried in air at 120°C for 8 hr, and reduced in flowing H_2 at 500°C for 1 hr. Residual impregnating solution combined with wash water was analyzed for Pt. Characterization as to the type of Pt profile was determined by visual observation or by electron probe microanalysis (EPM) of beads that had been cleaved in half (*30*). EPM was performed on an Acton MS-64 microprobe using a point count technique. Beads that had been cleaved in half were scanned across the flat side through the bead center. Thirty-second counts were taken at 100-μm intervals across the surface. Scans at one to four orientations were taken for each bead. Data smoothing consisted of averaging the scan data taken at all orientations and reporting the averaged and normalized Pt profile from bead center ($r/R = 0$) to surface ($r/R = 1$). Visual observation was used when the profile was obviously a shell or core type with a sharp boundary between Pt and bare support. EPM was used when the profile was diffuse.

More extensive coimpregnation studies using solutions prepared from various combinations of H_2PtCl_6, CA and NaBr stock solutions, and water of dilution were conducted in a manner similar to the above experiments; however, in the more extensive studies, the effects of impregnation time and NaBr and CA concentrations on final Pt profile were studied. EPM was used in determining Pt profiles for all samples.

RESULTS AND DISCUSSION

a. Adsorption Studies

Adsorption plays a large role in the impregnation of γ-alumina with H_2PtCl_6 solution. The bonding between Pt complex (henceforth referred to as Pt) and the surface is not well understood although mechanisms have been suggested. For example, recent studies have suggested that the adsorption of Pt is associated with either (1) variation of pH of the solution due to acid attack of the alumina with dissolution of surface aluminum ions (*25*), or (2) ligand displacement reaction of anionic Pt complexes with the alumina surface (*27*).

Figure 1 shows the total uptake of Pt after beads were contacted for 2 hr with impregnating solution containing H_2PtCl_6, then washed, dried, and reduced. The ordinate of this graph, "total Pt uptake," takes into account both adsorbed Pt and Pt deposited from pore solution during drying. The solid line shows the trend of the data. The dashed 45° line is a theoretical line for irreversible adsorption. The fact that data points at initial Pt values of about 0.006 mole and below fall near the theoretical line shows the strong interaction between Pt and γ-alumina. The other dashed line shows the trend of data at large values of initial Pt. The increase in the total Pt uptake in this linear region is due to Pt deposited from pore solution during drying. This increase can be used to determine the effective pore volume for the Pt in solution (*21, 31, 32*). The intersection of the two dashed lines represents the Pt uptake at saturation coverage of adsorption sites. The saturation coverage, 0.012 mmole Pt,

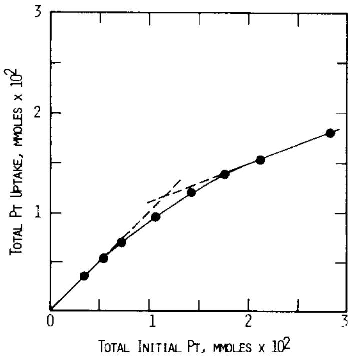

FIG. 1. Total uptake of Pt from impregnating solution by γ-alumina.

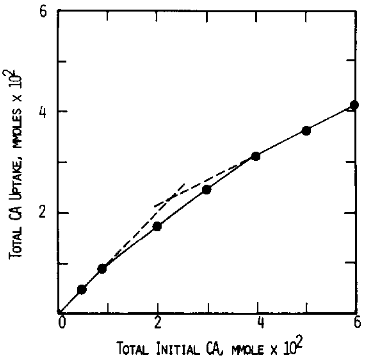

FIG. 2. Total uptake of CA from impregnating solution by γ-alumina.

divided by alumina sample weight and surface area corresponds to 110 μmole/g and 750 μmole/m^2, respectively.

Figure 2 is a similar graph for the total uptake of CA. As in the case of Pt, data points at low initial CA fall near the dashed 45° line thus showing a strong interaction betwen CA and γ-alumina; at large initial CA the data trend is linear. Intersection of the two dashed lines, which corresponds to saturation coverage of adsorption sites, occurs at 0.023 mmole CA. Saturation coverage divided by sample weight and surface area equals 215 μmole/g and 1433 μmole/m^2, respectively, or approximately twice the saturation coverage for Pt.

Adsorption isotherms (Fig. 3) were determined for both Pt and CA from data in Figs. 1 and 2 by subtracting the effective pore volume contribution from total uptake. The isotherms are expressed in terms of percent of adsorbed species. The line through the Pt data corresonds to the Langmuir equation:

$$\text{wt\% Pt} = \frac{2880C}{1 + 1330C}.$$

The CA data do not conform to the Langmuir model. A line was drawn, however, to show the trend of the data.

b. *Effect of Coingredients on Pt Profile*

Table 1 presents a list of acids and salts which were studied in a set of coimpregnation experiments. The purpose was to screen a large number of chemicals as coingredients with H_2PtCl_6 to determine their

TABLE 1

Properties of Coimpregnated Catalysts

Acid or salt	Impregnation time, 1 hr					Impregnation time, 22 hr		
	Conc (*M*)	Pt (wt%)	Pt band, *r*/*R*			Conc (*M*)	Pt (wt%)	Pt band
			Begins at	Ends at	Type			Type
None	—	0.51	1	0.77	1	—	0.51	2
$AlCl_3$	0.01	0.50	1	0.56	1	0.01	0.51	2
HCl	0.01	0.51	1	0.67	1	0.01	0.50	2
NaCl	0.01	0.49	1	0.81	1	0.01	0.51	2
HF	0.01	0.50	—	—	5	0.01	0.50	5
NaF	0.01	0.51	1	0.83	1	0.01	0.51	2
NaBr	0.01	0.50	1	0.77	1	0.01	0.50	9
HNO_3	0.01	0.50	1	0.50	1	0.01	0.51	3
$NaNO_3$	0.008	0.49	1	0.79	1	0.008	0.51	2
Na_3PO_4[a]	0.01	0.31	0.83	0	7	0.01	0.10	8
Na benzoate	0.01	0.48	1	0.78	1	0.01	0.50	2
Acetic acid	0.01	0.51	—	—	3	0.01	0.50	uniform
Citric acid	0.01	0.49	0.84	0.44	4	0.01	0.48	6
Na citrate[a]	0.02	0.19	0.33	0	7	0.01	0.14	8
Tartaric acid	0.01	0.49	—	—	6	0.01	0.51	7

[a] The 22-hr sample was prepared using a fresh solution of Na_3PO_4 (or Na citrate) and H_2PtCl_6 while the 1-hr sample was prepared using a portion of that same solution after it had been stored for 2 or 3 days.

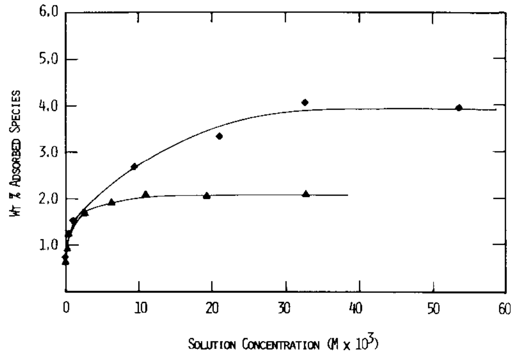

FIG. 3. Adsorption isotherms (25°C) for Pt (▲) and CA (◆).

effects upon the final Pt profile in the alumina beads. It was desirable to examine these effects after relatively short (1 hr) and long (22 hr) impregnation times, and to eliminate profile changes over this time period due to Pt diffusing into the pores from external impregnating solution. To avoid this undesireable effect, the total amount of Pt and total volume of solution were kept low—total Pt in solution was about 23% of the amount required to saturate the adsorption sites in the alumina (Fig. 1); solution volume was about 2.7 times the pore volume. Under these conditions, at short impregnation time, the solution would become essentially depleted of Pt as the Pt adsorbed on the support thus substantially reducing any driving force for diffusion. A control experiment in which no coingredient (Table 1, first entry) was added to the solution confirmed these expectations: after 1 hr of contact, the resulting catalyst contained a sharply defined shell of adsorbed Pt. After 22 hr of contact, the Pt shell showed only slight dispersion at the inner boundary.

In most experiments the coingredient concentration was 0.01 *M*, which corresponds to a coingredient to Pt mole ratio of 1.77. The columns in Table 1 labeled "type" refer to types of profiles which were produced in these experiments after impregnated beads had been dried and reduced. Schematic representations which most closely describe these profiles are shown in Fig. 4. These representations can be described in qualitative terms as follows:

Type 1—Outer shell, sharply defined
Type 2—Outer shell, diffuse
Type 3—Outer shell, diffuse to center
Type 4—Inner shell, sharply defined
Type 5—Inner shell, diffuse
Type 6—Inner shell, diffuse to center
Type 7—Core, sharply defined
Type 8—Core, diffuse
Type 9—Linearly increasing from center

For those catalysts which have sharply defined boundaries between regions with and without Pt, such as types 1, 4, and 7, the Pt bandwidth depended upon the coingredient, as shown in Table 1. With the exceptions of HF, acetic acid, and tartaric acid, all coingredients produced sharply defined Pt profiles after 1 hr of impregnation. Of these coingredients only CA and tartaric acid produced an inner Pt shell, and Na citrate, a Pt core. After 22 hr of impregnation, the Pt profiles produced with $AlCl_3$, HCl, NaCl, NaF, $NaNO_3$, and Na benzoate showed only slight dispersion at the inner boundaries. This finding illustrates the near irreversibility of the adsorption of Pt on alumina. With the exception of catalysts prepared with coingredients Na_3PO_4 and Na citrate, the weight percent of Pt in the

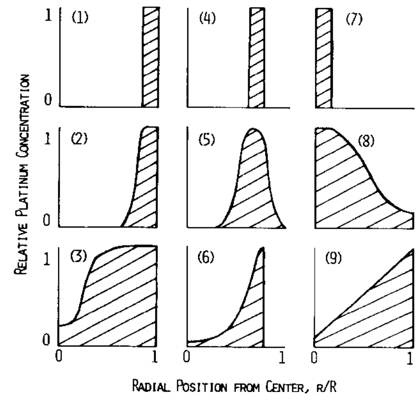

FIG. 4. Types of Pt profiles obtained in coimpregnation experiments.

final catalyst represented greater than 95% total Pt uptake from solution.

Maatman (11) discussed the roles played by competitive adsorbates in distributing Pt throughout η-alumina supports. Michalko (13, 14) showed that dibasic acids, especially CA, could be used with H_2PtCl_6 to produce shell or core profiles. Becker and Nuttall (12) studied the influence of process variables on Pt profiles when CA was used with H_2PtCl_6. It is interesting to note that in Becker and Nuttall's work, impregnation time was an important variable–relatively short (e.g., 5 min) impregnation times produced sharp inner shell profiles, whereas 30-min impregnation time produced very diffuse almost uniform Pt profiles. Maatman (11) also reported near uniform Pt profiles after several-hour impregnation times with various coingredients. In the present experiments, with most of the coingredients, impregnation time had less of an effect on Pt profiles than in previous works for reasons previously discussed. For catalysts produced with coingredients NaBr, HNO_3, Na_3PO_4, acetic acid, CA, Na citrate, and tartaric acid, increasing the impregnation time had a significant effect on Pt profile, although only acetic acid produced a uniform Pt profile at 22 hr. Figure 5 shows an example of a profile produced by coimpregnation with NaBr for 24 hr followed by drying and reduction. Figure 5 shows the typical data scatter that occurred in all EPM scans.

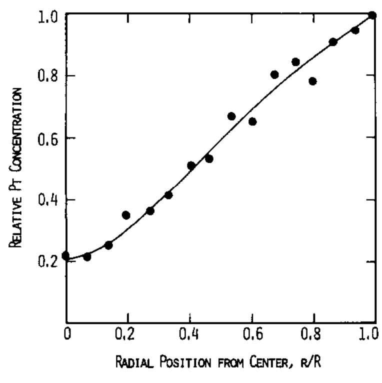

FIG. 5. Pt profile produced by coimpregnation of alumina beads with NaBr and H_2PtCl_6. Initial NaBr : Pt mole ratio, 1.77 : 1; impregnation time, 24 hr; Pt content of beads, 0.50 wt%.

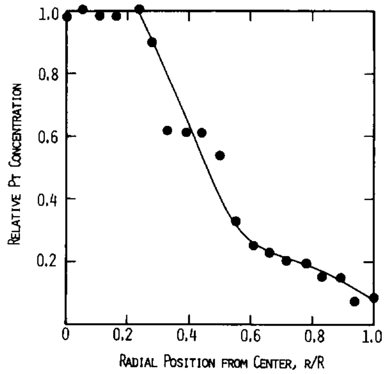

FIG. 6. Core Pt profile produced by coimpregnation of γ-alumina beads with CA and H_2PtCl_6 solution. Initial CA : Pt molar ratio, 5.31 : 1; impregnation time, 24 hr; Pt content of beads, 0.50 wt%.

An additional series of coimpregnation experiments were run with CA at a concentration of 0.03 *M* and a CA to Pt mole ratio of 5.31. This concentration was used in order to produce a core instead of an inner shell. The resulting core profiles showed slight dispersion at the boundary for low impregnation times. Pt dispersion increased substantially at higher impregnation times; however, even at times on the order of 24 hr, profiles maintained the broad flat center which typifies a core profile (see Fig. 6).

c. *Effect of NaBr on the Pt Profile*

NaBr was the only coingredient which produced a monotonically increasing Pt profile from bead center to surface (Fig. 5). It was therefore subjected to further investigation.

Table 1 shows that NaBr had no effect on the 1-hr profile compared to the control, but had a great effect on the 22-hr profile. It appears that during the coimpregnation process, Pt adsorbed rapidly to form an outer shell catalyst; then in a comparatively slow process the NaBr interacted with the Pt or surface. This interaction increased the mobility of the Pt and allowed it to diffuse toward the center.

This simple model led to the idea of using three ingredients—NaBr, CA, and

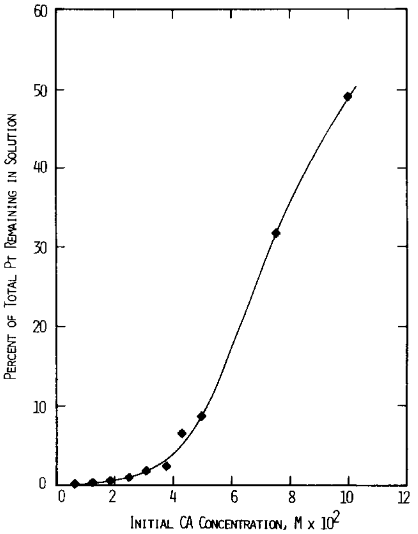

FIG. 7. Effect of CA concentration on uptake of Pt from solution. Initial Pt concentration, 2.8 × 10^{-3} *M*; ratio of liquid volume to alumina weight, 7.5 ml/g.

H_2PtCl_6—in impregnating solution as a means of producing monotonically decreasing Pt profiles. The reasoning used was as follows: It is known that CA interacts strongly with γ-alumina (Fig. 2) and successfully competes with Pt for adsorption sites to form core Pt profiles. If during the impregnation experiment, the core profile is first established and later modified by the relatively slow interaction between NaBr and adsorbed Pt, monotonically decreasing profiles might be achieved.

Figure 7 shows that high CA concentrations can severely reduce the total uptake of Pt from aqueous solution by γ-alumina. It was therefore important in these catalyst preparation experiments to adjust the CA to Pt ratio sufficiently high to effect a core but low enough so that high Pt uptake was maintained.

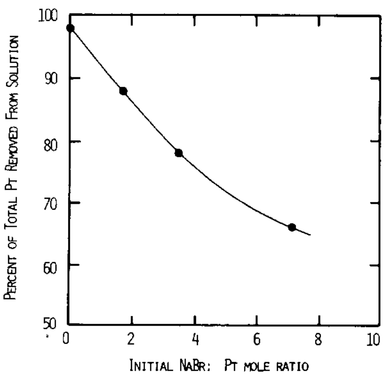

FIG. 8. Effect of NaBr content on total Pt uptake by alumina beads. Initial CA : Pt mole ratio, 5.31 : 1, impregnation time, 24 hr.

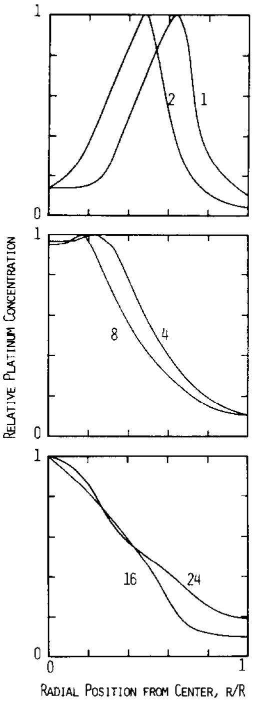

FIG. 9. Effect of impregnation on Pt profile for NaBr : CA : Pt mole ratio 1.77 : 5.31 : 1. Impregnation times (hr) are shown on the figure.

Figure 8 shows that high NaBr concentrations can also reduce total uptake of Pt from impregnating solutions. It was therefore important in these catalyst preparation experiments to adjust the NaBr to Pt ratio high enough so that it caused the Pt profile to move but low enough so that high Pt uptake was maintined.

Figure 9 shows the relative Pt concentration profiles for coimpregnation experiments as a function of impregnation time. For these particular experiments, the solution contained NaBr, CA, and Pt in the molar ratio 1.77 : 5.31 : 1. (The lines represent smooth curves drawn through the EPM data to show the data trend.)

Figure 10 shows the EPM data for the 16-

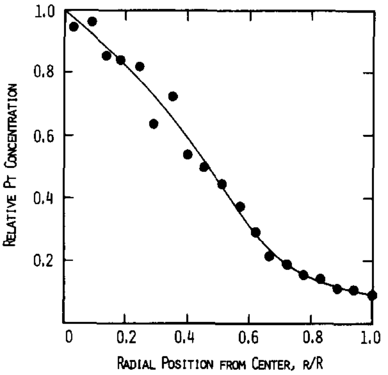

FIG. 10. Pt profile produced by coimpregnation of γ-alumina beads with NaBr, CA, and H_2PtCl_6 solution. Initial NaBr : CA : Pt mole ratio, 1.77 : 5.31 : 1; impregnation time, 16 hr; Pt content of beads, 0.50%.

hr sample. The interesting effect of the NaBr is that it produces a monotonically decreasing profile which has a sharp maximum at the bead center as opposed to a broad flat center as in Fig. 6.

CONCLUSIONS

NaBr, when used as a coingredient in H_2PtCl_6 or CA–H_2PtCl_6 impregnating solutions, is effective in modifying the Pt distribution within γ-alumina supports. Pt profiles which result from the above solutions are respectively monotonically increasing and monotonically decreasing from bead center to surface. Without the NaBr coingredient the above solutions produce shell- and core-type Pt profiles respectively. The function of the NaBr is unclear although it appears to interact with the adsorbed Pt or surface and weaken the Pt–surface bond.

ACKNOWLEDGMENTS

This work is supported by the National Science Foundation Grant ENG 78-00731. The authors wish to express appreciation to Mr. J.-P. Fort, Rhône-Poulenc Inc., who provided the catalyst supports.

REFERENCES

1. Becker, E. R., and Wei, J., *J. Catal.* **46**, 365 (1977).
2. Becker, E. R., and Wei, J., *J. Catal.* **46**, 372 (1977).
3. Corbett, W. E., and Luss, D., *Chem. Eng. Sci.* **29**, 1473 (1974).
4. Kasaoka, S., and Sakata, Y., *J. Chem. Eng. Jap.* **1**, 138 (1968).
5. Shadman-Yazdi, F., and Petersen, E. E., *Chem. Eng. Sci.* **27**, 227 (1972).
6. Villadsen, J., *Chem. Eng. Sci.* **31**, 1212 (1976).
7. Ernst, W. R., and Daugherty, D. J., *AIChE J.* **24**(5), 935 (1978).
8. Ernst, W. R., and Wei, J., *J. Catal.* **39**, 303 (1975).
9. Dwyer, F. G., Eagleton, L. C., Wei, J., and Zahner, J. C., *Proc. Roy. Soc. Ser. A* **302**, 253 (1968).
10. Oleck, S. M., U.S. Patent 2,884,382, April 28, 1959.
11. Maatman, R. W., *Ind. Eng. Chem.* **51**(8), 913 (1959).
12. Becker, E. R. and Nuttall, T. A., *in* "Preparation of Catalysts II: Proceedings of the Second International Symposium on Scientific Bases for the Preparation of Heterogeneous Catalysts" (B. Delmon et al., Eds.) Louvain-la-Neuve, Belgium, 1978, Elsevier Scientific, Amsterdam Holland 1979.
13. Michalko, E., U.S. Patent 3,259,454, July 5, 1966
14. Mickalko, E., U.S. Patent 3,259,589, July 5, 1966.
15. Cervelló, J., Gardia de la Banda, J. F. Hermana, E., and Jiménez, J. F., *Chem. Eng. Technol.* **48**, 520 (1976).
16. Chen, H. C., and Anderson, R. B., *Ind. Eng. Chem. Prod. Res. Develop.* **12**(2), 122 (1973).
17. Santacesaria, E., Galli, C., and Carrá, S., *React. Kinet. Catal. Lett.* **6**(3), 301 (1977).
18. Summers, J. C., and Hegedus, L. L., *J. Catal.* **51**, 185 (1978).
19. Harriott, P., *J. Catal.* **14**, 43 (1969).
20. Vincent, R. C., and Merrill, R. P., *J. Catal.* **35**, 206 (1974).
21. Maatman, R. W., and Prater, C. D., *Ind. Eng. Chem.* **49**(2), 253 (1957).
22. Petró, J., *in* "Contact Catalysis" (Z. G. Szabó and D. Kalló, Eds.), Vol. 2, p. 47. American Elsevier, New York, 1976.
23. Dorling, T. A., Lynch, B. W. J., and Moss, R. L., *J. Catal.* **20**, 190 (1971).
24. Santacesaria, E., Gelosa, D., and Carrá, S., *Ind. Eng. Chem. Prod. Res. Develop.* **16**(1), 45 (1977).
25. Santacesaria, E., Carrá, S., and Adami, I., *Ind. Eng. Chem. Prod. Res. Develop.* **16**(1), 41 (1977).
26. Maatman, R. W., Mahaffy, P., Hoekstra, P., and Addink, C., *J. Catal.* **23**, 105 (1971).
27. Summers, J. C., and Ausen, S. A., *J. Catal.* **52**, 445 (1978).
28. Parfitt, G. D., *Pure Appl. Chem.* **48**, 415 (1976).
29. Sandell, E. B., "Colorimetric Determination of Traces of Metals," 3rd ed. Interscience, New York, 1959.
30. Roth, J. F., and Reichard, T. E., *J. Res. Inst. Catal. Hokkaido Univ.* **20**(2), 85 (1972).
31. Maatman, R., Poel, M., and Mahaffy, P., *J. Colloid Interface Sic.* **48**, 134 (1974).
32. Giddings, J. C., Kucera, E., Russell, C. P., and Myers, M. N., *J. Phys. Chem.* **72**, 4397 (1968).