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Impregnating Chromium and Copper in Alumina

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The impregnation of spheres of alumina with aqueous solutions of chromium III nitrate and/or copper II nitrate was studied. The solutions were added to the alumina individually, mixed, and sequentially. Chromium III nitrate was strongly adsorbed on the alumina and deposited near the outside of the sphere. Copper II nitrate was less strongly adsorbed and penetrated deeper than the chromium solution. In sequential impregnations, Cr displaced Cu toward the center of the sphere, but Cu moved past Cr initially added to the alumina.

In preparing impregnated catalysts, the dried porous support is immersed in a given volume of solution of known concentration for the desired time and then dried and calcined. The impregnation step seems reasonably simple with the solution drawn into the pores by capillary action, adsorbing on the pore walls as it enters. Diffusion of the solute may also be appreciable, particularly if the time before drying is long. Mathematical descriptions of the impregnation step have been given (*1*, *2*). The drying and calcining steps involve heat and mass transfer and often chemical reaction, and the extent to which the solute redistributes is not known. The preparation of impregnated catalysts has been reviewed (*3*, *4*), and two symposia were devoted to this subject (*5*, *6*). Summers and Hegedus modified impregnation procedures to produce platinum-palladium-on-alumina catalysts with one metal deposited near the periphery of the particle and the other inside, both metals near the periphery and both inside (*7*). These catalysts were tested for activity and durability in oxidizing automotive exhaust. Summers and Ausen investigated the impregnation process and studied interactions of noble-metal complexes with alumina (*8*). Chen and Anderson (*2*, *9*) have determined concentration profiles for chromium-on-alumina and copper-on-alumina using the electron probe microanalyzer (EPMA). Chromium III nitrate was more strongly adsorbed and penetrated less deeply than CrO_3, ammonium chromates, and copper II nitrate. Uses of EPMA in catalysis have been reviewed (*10*).

The present paper describes catalysts prepared by impregnating alumina spheres with aqueous solutions of chromium III nitrate and/or copper II nitrate, individually, sequentially, or as a mixed solution. After impregnation some spheres were stored in ambient laboratory air at room temperature for 1 or 2 weeks to study diffusion in the pore solution. Concentration profiles were made on sectioned particles by EPMA.

EXPERIMENTAL METHODS

γ-Alumina spheres, furnished by Kaiser Chemicals, of 5.5-mm diameter were heated for 1 h at 300°C and held in air in an oven at 95°C for weeks until used. The impregnation procedure was essentially the same as described previously (*2*, *9*), except that the volume of solution was 0.8 of the pore volume in all cases. The solution was added to the dried support with a syringe as

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rapidly as absorbed; typical times of impregnation were 5 min for copper nitrate and 7 min for chromium nitrate.

The catalysts were dried in air at 150°C for 8 h, and there was no calcining step. Some samples were dried at 150°C immediately after impregnation; other preparations were stored in the ambient air at room temperature for 7 or 14 days before drying. A series of catalysts were prepared by impregnating first with one solution and then with the other. In one set the samples were dried at 150°C after the first impregnation and again after the second. In the other set the pellets were stored 7 days in ambient air at room temperature after the first impregnation and were stored another 7 days after the second impregnation before drying. The following notations are used: CuOD means impregnated with copper nitrate solution, stored for 0 day before drying, i.e., dried immediately, and Cu7Cr7D means impregnated with copper nitrate solution, stored in air for 7 days, impregnated with chromium nitrate solution, stored in air for 7 days, and dried at 150°C. Weight changes in the preparation steps were determined. Table 1 gives the concentrations of the solutions and the sequence of addition of the solutions and the storage and drying steps.

Particles were mounted in plastic and cut to reveal their cross section by usual metallurgical methods (*9*). The polished sections were flat on a scale of micrometers except for pits of varying size, up to 0.4 mm, and number. An Acton electron probe microanalyzer was used as described previously (*2*, *9*). Concentrations are presented as weight ratios of Cr or Cu to Al, because the concentration of Al should remain constant. The pits in the polished section caused some points of the concentration profiles to scatter widely; for this reason the profiles were smoothed (mathematically) (*11*). Color photomicrographs were made of the sectioned particles.

EXPERIMENTAL RESULTS AND DISCUSSION

In the present experiments the alumina

TABLE 1

Preparation and Composition of Catalyss

Figure	Metal	Designation on graphs	Preparation sequence	Solution used[a]	Metal content ($g/g\ Al_2O_3$) Introduced	Metal content ($g/g\ Al_2O_3$) Found
1A	Cr	——	CrOD	a	0.0304	0.0169
1A	Cr	– – –	Cr14D	a	0.0304	0.0342
1B	Cu	–-–-	CuOD	b	0.0435	0.0493
1B	Cu	······	Cu14D	b	0.0443	0.0572
2A	Cr	——	(Cu + Cr)OD	c	0.0154	0.0161
	Cu	–-–-			0.0217	0.0215
2B	Cr	– – –	(Cu + Cr)14D	c	0.0154	0.0199
	Cu	······			0.0222	0.0182
3A	Cr	——	CrODCuOD	a	0.0308	0.0305
	Cu	–-–-		b	0.0435	0.0507
3B	Cr	– – –	Cr7Cu7D	a	0.0305	0.0266
	Cu	······		b	0.0443	0.0373
4A	Cu	–-–-	CuODCrOD	b	0.0435	0.0471
	Cr	——		a	0.0309	0.0278
4B	Cu	······	Cu7Cr7D	b	0.0442	0.0426
	Cr	– – –		a	0.0305	0.0354

[a] 1.6 F $Cr(NO_3)_3$; (b) 1.9 F $Cu(NO_3)_2$; (c) 0.8 F $Cr(NO_3)_3$ + 0.95 F $Cu(NO_3)_2$.

used was the same as in the previous work (*2*, *9*) except that it had been dried at 300°C for 1 h and for an extended period at 95°C rather than being heated at 600°C. The properties of the aluminas from N_2 isotherms at -195°C were:

	Heat treatment (°C)	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diam (Å)
Present work	300 (1 h) 95 (weeks)	367	0.459	35
Previous work (*2*, *9*)	600 (20 h) 215 (weeks)	125	0.450	72

The pore volume did not change very much, but the surface area of the sample used in the present paper was three times that of the previous alumina. A second difference between the present and previous work was that the volume of solution impregnated was 80% of the pore volume. Therefore, if the solution penetrated uniformly, it would reach only about half-way to the center of the sphere. Movement of the solute during storage and/or drying should be readily apparent. In some instances the alumina spheres were impregnated with solutions containing both chromium and copper nitrates.

A third difference was that some samples were stored at room temperature in the ambient air for 1 or 2 weeks before further treatment. In this period diffusion and movement of the solution may occur, and water was lost by evaporation. In some experiments after a week of storage at room temperature, the granule was impregnated with the other reagent. The solutions in the pores evaporated at about half the rate of pure water. The loss of water by evaporation was not sufficient for the alumina to accommodate the volume of the second impregnation, 0.8 of the pore volume; thus, the particles were wet with solution after the second impregnation.

A fourth difference was that the spheres were dried in air at 150°C rather than being calcined at 600°C. At 150°C copper II nitrate dehydrated but did not decompose. Chromium III nitrate decomposed apparently to a hydrated oxide at this temperature, the color of the impregnated spheres changing from dark purple to brown. The sections of the spheres were colored, and optical micrographs in color were made. The colors corresponded to the electron microprobe profiles reasonably.

A consequence of the use of the higher-area alumina and the smaller amount of solution was that the concentration profiles were often less symmetrical than those obtained in the previous work (*2*, *9*). Furthermore, the electron microprobe traverse (usually only one was made) may not yield the correct average concentration. The agreement of the amounts of Cu and Cr introduced and found (Table 1) are in a few instances poor.

Figures 1 to 4 show concentration profiles for Cr and Cu, expressed as weight ratios of metal to Al, obtained by the EPMA on sectioned impregnated spheres. Shown on the abscissa by ∧ is the depth to which the solution would penetrate if the structure were uniform. Figure 5 presents the size of the distinct colored zones observed in the optical micrographs. A good correspondence between the colored zones and the EPMA data was obtained on the following basis: dark brown, DB, was associated with high Cr concentrations or moderate to high concentrations of both Cr and Cu; light brown, B, for moderate concentrations of Cr; and blue, Bl, for Cu. The brown color of Cr obscured the blue of Cu, if both were present.

Weight changes were determined on particles impregnated with aqueous solutions of copper II or chromium III nitrates and heated at 150°C. For the copper salt the weight changes corresponded to the formation of anhydrous copper II nitrate. The residium from chromium nitrate weighed about half of that calculated for the anhydrous nitrate but more than the weight expected for the formation of a variety of anhydrous oxides of chromium.

The viscosities of these solutions are

large and may be a pertinent factor in determining the depth of penetration. The following viscosities were determined in a Ubbelohde viscosimeter: 1.6 *F* chromium III nitrate, 3.4 cP; 1.9 *F* copper nitrate, 1.9 cP; and a 1/1 mixture of the two solutions, 2.5 cP.

Many of the concentration profiles can be explained simply; a few are complicated. In Fig. 1B for impregnation and immediate drying (CuOD), the Cu penetrated to about 1 mm from the center, somewhat beyond the volume that should be filled in a uniformly porous solid, indicated by Λ. This depth for the Cu solution may be considered a minimum value for the penetration of the water from any solution. In Fig. 1A, CrOD, Cr penetrates only a short distance corresponding to about half the pore volume. The concentration of Cr in this layer is large, about 1.6 times that of the original solution if the concentration were uniform. The Cr diffused inward only a small distance on standing in air for 14 days before drying, Cr14D (Fig. 1A), but in similar tests (Fig. 1B) Cu diffused inward significantly. The immobility of Cr may be attributed to strong adsorption on the alumina, and the large viscosity of the solutions of $Cr(NO_3)_3$ restricts the initial penetration. Copper nitrate is less strongly adsorbed and has a smaller viscosity.

When both chromium and copper nitrates are present in the solution, the penetration of Cr is increased and that of Cu decreased, as shown in Fig. 2A for (Cu + Cr)OD, where both solutes penetrate to about the arrow. In Fig. 2B, after 14 days in air and drying, (Cu + Cr)14D, the Cr and Cu form two distinct overlapping peaks, the one for chromium nearer the outside. The dark brown in Fig. 5 is found at about the intersection of the curves. Cu did not penetrate deeper into the particle in the 2 weeks in air.

In Fig. 3, a volume of $Cr(NO_3)_3$ solution corresponding to 0.8 of the pore volume was added first, followed by the same volume of $Cu(NO_3)_2$; in Fig. 3A the specimen was dried at 150°C immediately after each impregnation, CrODCuOD, and in Fig. 3B after the addition of Cr, the sample was stored in air for 7 days, the second component added, followed by storing in air for another 7 days before drying at 150°C, Cr7Cu7D. In Fig. 3A after the first drying the Cr profile was similar to the corresponding curve in Fig. 1A, but the chromium nitrate was largely decomposed to a hy-

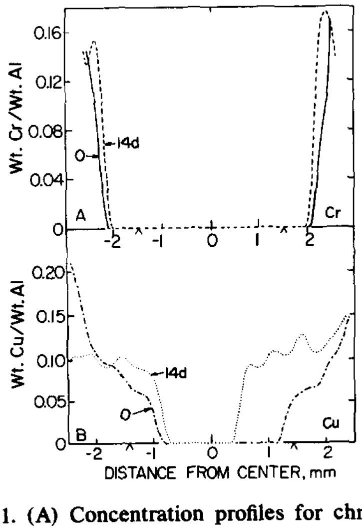

FIG. 1. (A) Concentration profiles for chromium: dried immediate, ——; dried after 14 days, – – –. (B) Concentration curves for copper: dried immediately, – – –; after 14 days, · · · · ·.

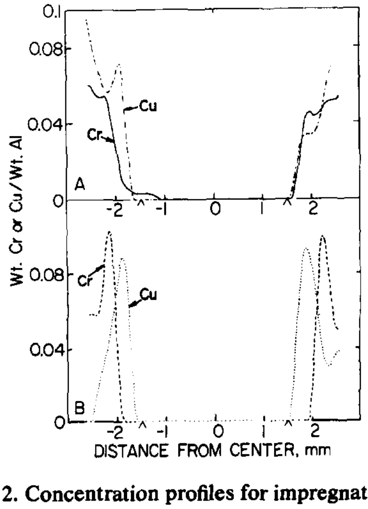

FIG. 2. Concentration profiles for impregnation with a mixed solution of chromium III nitrate and copper II nitrate. (A) Dried immediately, Cr, ——; Cu, – – – –. (B) Dried after 14 days, Cr, – – –; Cu, · · · · ·.

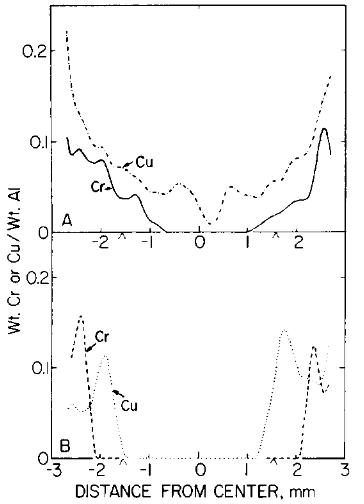

FIG. 3. Profiles for sequential addition of solutions. (A) Chromium III nitrate added first, dried immediately, copper II nitrate added and dried immediately; Cr, ——; Cu, ----. (B) Cr added first, allowed to stand 7 days, Cu added and allowed to stand 7 days before drying; Cr, ---; Cu, · · · · ·.

drated oxide in drying at 150°C. The Cu solution then flowed past the Cr deposit and to the center of the particle. The Cu solution also redissolves the chromium deposit and carries Cr further into the particle, to give the deepest penetration of Cr in these experiments, and the movement of Cu to the center. Explanation of some aspects of Fig. 3A is difficult.

The profile in Fig. 3B (Cr7Cu7D) is similar to Fig. 2B. After the first impregnation, (Fig. 3B) the profile for Cr should be like that in Fig. 1A with the $Cr(NO_3)_3$ in the outer 50% of the volume. The Cu from the second impregnation moves past the Cr without displacing it inward appreciably. In the 7 days in ambient air only part of the water in the solution of $Cr(NO_3)_3$ was evaporated.

Figure 4 depicts sequential addition of the impregnants similar to Fig. 3, except that the Cu solution was added first in Fig. 4. For Fig. 4A, the Cu profile should be similar to the corresponding one in Fig. 1B after the first drying at 150°C. The $Cr(NO_3)_3$ then penetrates a little deeper than in Fig. 1A and displaces the Cu inward producing a concentration peak, but the depth of penetration of Cu was not larger than in Fig. 1B.

In Fig. 4B the initial Cu impregnation after 7 days should be similar to the dotted curve of Fig. 1B with copper penetrating to within about 0.5 mm of the center. The Cr addition displaces the Cu from the outer layer to the center of the particle, and Cr penetrates deeper into the particle than in Figs. 1A and 2B.

Pertinent steps in the present preparations are: (a) the initial penetration of the solution into the dry porous sphere, (b) chemisorption of the solute on the support, (c) diffusion of the solute in the solution in the pores, and (d) drying at 150°C. Most preparations, but not those described in the present paper, also include a calcination step.

The viscosity of the solution determines the rate of penetration into the support and may influence diffusion. As the solution penetrates the particle, chemisorption occurs on the pore walls. In the period before drying, diffusion occurs in the solution in the pores. Although diffusivities may be a function of viscosity, viscosity should not limit the ultimate depth of penetration of

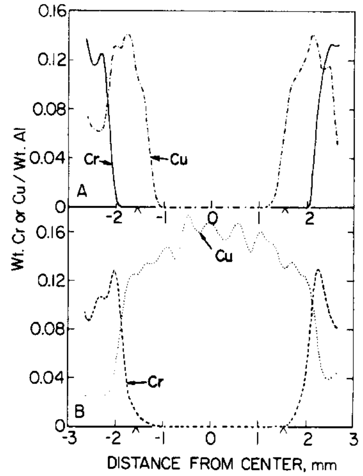

FIG. 4. Profiles for sequential addition of solutions. (A) Copper II nitrate added first, dried immediately, chromium III nitrate added, dried immediately; Cr, ——; Cu, ----. (B) Cu added first and allowed to stand for 7 days, Cr added and allowed to stand for 7 days before drying; Cr, ---; Cu, · · · · ·.

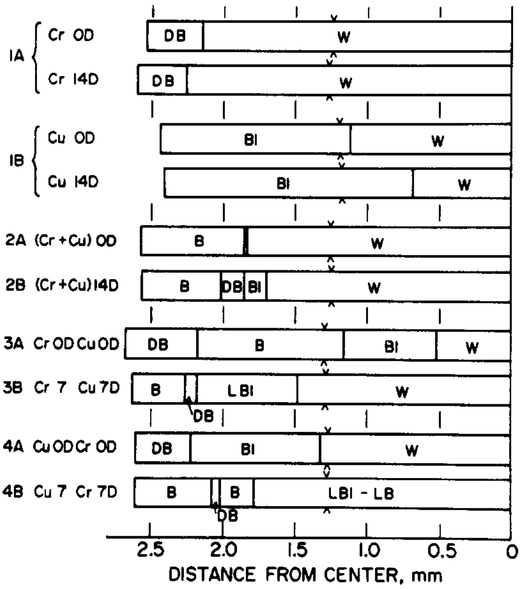

FIG. 5. Histograms showing colored zones in micrographs. Figure numbers for corresponding concentration profiles are shown at the left side. B, Brown; Bl, blue; W, white; D, dark; and L, light.

the solute because the viscosity of the solution diminishes to that of water when the concentration of solute approaches zero. Drying seems more complicated than previous steps because it also involves temperature gradients. On a macroscale, at least, there is little tendency for evaporation to occur at the pore mouths with the solution being "pumped out" of the pores and the solute deposited near the pore mouth. For ammonium chromate on alumina (*2*) the quantity of Cr near the periphery of the particle equaled the amount chemisorbed plus the amount that was in the pore solution at the periphery before drying.

The chromium III nitrate species, probably of a partly hydrolyzed complex, polymeric nature, are very strongly adsorbed on the alumina, and even in 14 days, penetrates only a short distance. These chromium solutions are very viscous but this should not be a limiting factor determining depth of penetration. Copper II species are also chemisorbed but less strongly than chromium III, and the copper diffused inward an appreciable distance in 14 days.

In drying in air at 150°C, the copper II nitrate solution in the support merely dried and dehydrates, but the chromium III nitrate decomposes to a hydrated oxide, possibly with oxidation of Cr to a higher valence. This chromium deposit is soluble in the copper II nitrate solution and seems more mobile than the original chromium nitrate solution in the support merely dries penetrated deeper than chromium III nitrate (*9*).

Our data give no indication of compound formation between copper and chromium. The chromium III species will displace the copper II; the two species tend to separate on standing, forming two partly overlapping concentration peaks with the copper peak nearer the center. The strongly adsorbed chromium III species do not plug or block the pores of the support; the copper species can penetrate or diffuse through the zone occupied by chromium.

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REFERENCES

1. Vincent, R. C., and Merrill, R, P., *J. Catal.* **35**, 206 (1974).
2. Chen, H-C., and Anderson, R. B., *J. Catal.* **43**, 200 (1976).
3. Ciapetta, F. G., and Plank, C. J., *in* "Catalysis" (P. H. Emmett, Ed.), Vol. 1, pp. 318–319, 343–344. Reinhold, New York, 1954.
4. Moss, R. L., *in* "Experimental Methods in Catalytic Research" (R. B. Anderson and P. T. Dawson, Eds.), Vol. 2, Chap. 2. Academic Press, New York, 1976.
5. Delmon, B., Jacobs, P. A., and Ponclet, G. (Eds.), "Preparation of Catalysts." Elsevier, Amsterdam/New York.
6. Delmon, B., *et al.*, Eds., Preparation of catalysts II, *in* "Proceedings of the Second International Symposium on the Scientific Bases for the Preparation of Heterogeneous Catalysis." Elsevier, Amsterdam/New York, 1979.
7. Summers, J. C., and Hegedus, L. L., *J. Catal.* **51**, 185 (1978).
8. Summer, J. C., and Ausen, S. A., *J. Catal.* **52**, 445 (1978).

9. Chen, H-C., and Anderson, R. B., *Ind. Eng. Chem. Prod. Res. Develop.* **12**, 122 (1973).
10. Purdy, G. R., and Anderson, R. B., *in* "Experimental Methods in Catalytic Research" (R. B. Anderson and P. T. Dawson, Eds.), Vol. 2, Chap. 3. Academic Press, New York, 1976.
11. Hershey, H. C., Zakin, J. L., and Sinha, R., *Ind. Eng. Chem. Fundam.* **6**, 413 (1967).