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Concentration Profiles in Impregnated Chromium and Copper on Alumina

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Chromium and copper catalysts were prepared by adding known amounts of aqueous solutions of chromium and copper compounds to dry γ-alumina spheres. After drying and calcining, the spheres were sectioned, and concentration profiles were determined along the diameter of the circular cross section by an electron probe microanalyzer. Isotherms for the adsorption on the alumina of aqueous solutions of ammonium chromate and ammonium dichromate were determined.

Concentration profiles were functions of the solute and the concentration and amount of solution. It is inferred that the order of adsorption on the alumina of aqueous solutions is: chromium III nitrate > copper II nitrate > chromic acid > ammonium dichromate > ammonium chromate = copper II ammine nitrate. Moderately accurate quantitative analyses can be made on impregnated catalysts with the electron probe; the amount of metal found was usually within 10% of the amount introduced.

The electron probe microanalyzer, despite its limited resolution of about 3 μm, has proved a useful tool in examining catalysts (*1-3*). This instrument is particularly suitable for studying fouling and poisoning of catalysts and in examining impregnated catalysts, as it provides a concentration profile for each element with atomic numbers larger than 10. Often qualitative or semiquantitative concentration profiles are adequate and a number of papers have reported oscilloscope displays or uncorrected scanning data on sectioned particles. Quantitative analyzes of moderate accuracy are possible, and Roth and Reichard (*4*) and the present authors (*5*) have reported quantitative concentration curves.

In preparing impregnated catalyst, the dried and sometimes evacuated porous support is immersed in given volume of solution of known concentration for a desired period of time, and then dried and calcined (*6*). Moss (*7*) has described the preparation of this type of catalyst in detail. The impregnation step seems reasonably straightforward with the solution drawn into the pores by capillary action, adsorbing on the pore walls as it enters. Diffusion of solute may occur, particularly if the time before drying is long. A reasonable mathematical description of the impregnation step has been given (*8*). The drying step involves heat and mass transfer in a complicated way, and it is not known if the solute redistributes in this operation.

The present paper extends the work previously reported on chromia-on-alumina (*5*) to include ammonium chromate and dichromate as impregnants and adsorption isotherms for these solutions, and copper II nitrate and $Cu(NH_4)_4(NO_3)_2$ on the same alumina.

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EXPERIMENTAL METHODS

γ-Alumina spheres, furnished by Kaiser Chemicals, with an average diameter of 5.5 mm were calcined in air at 600°C and stored in air at 215°C until used. After this treatment, the alumina has a surface area of 125 m^2/g, a pore volume of 0.45 cm^3/g, and an average pore diameter from ratio of pore volume to area of 72 Å. Known volumes of solution were added to individual particles that had been dried and weighed. The volume of solution was:

a. Equal to the pore volume (PV),
b. Half of the pore volume (HPV),
c. 20 ml/particle (XS).

For PV and HPV preparations an alumina sphere was placed on a glass plate and surrounded by a short section of glass tubing of about 5.7 mm i.d. that had been ground flat at the bottom end. The desired amount of solution was then introduced at the top of the particle with a hypodermic syringe. The rate of addition was varied to maintain a "wet" appearance of the particle without the solution dripping off the particle. All of the solution was absorbed by the particle, and the concentration profiles of particles sectioned at random directions to the addition were always very nearly symmetrical. The time required for addition varied from 5 to 10 min, the time increasing with increasing viscosity of the solution. The PV and HPV preparations were immediately

TABLE 1

Metal Content of Catalyst; Comparison of Amounts Introduced and Found

Fig.	Preparation type[a]	Solution (M)		Metal content ($g/g\ Al_2O_3$)	
				Introduced	Found[b]
1	PV	1.7	CrO_3	0.0399	0.0487
—[c]	PV	2.5		0.0596	0.0658
—[c]	XS	2.5		nd[d]	0.1147
1 2	PV	1.8	$Cr(NO_3)_3$	0.0429	0.0426
—[c]	XS	1.8		nd	0.0468
—[c]	PV	1.2		0.0287	0.0307
—[c]	XS	1.2		nd	0.0341
—[c]	PV	0.6		0.0143	0.0160
—[c]	XS	0.6		nd	0.0202
1, 3B	PV	0.8	$(NH_4)_2Cr_2O_7$	0.0414	0.0419
3B	HPV	0.8		0.0206	0.0181
3A	PV	0.8	$(NH_4)_2CrO_4$	0.0207	0.0184
3A	HPV	0.8		0.0103	0.0096
5	PV	1.6	$Cu(NO_3)_2$	0.0504	0.0313
5	HPV	1.6		0.0252	0.0237
5	PV	0.3	$Cu(NH_3)_4(NO_3)_2$	0.0094	0.0100
5	HPV	0.5		0.0047	0.0041

[a] Volume of solution used in impregnation: PV, equal to pore volume; HPV, half of pore volume; XS, excess solution; see Experimental Methods.
[b] Found by electron probe microanalyzer.
[c] From curves in Ref. (5).
[d] Not determined.

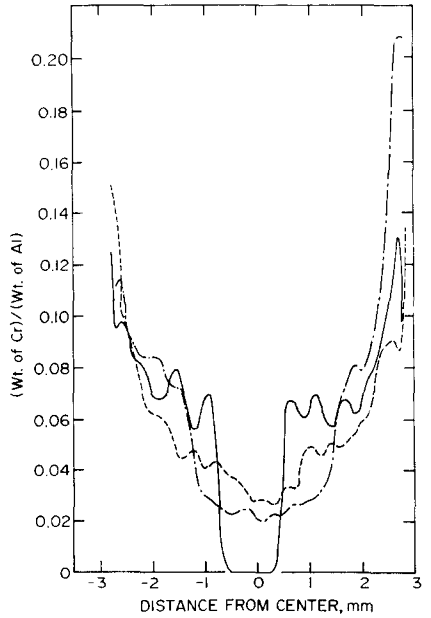

FIG. 1. Concentration curves for catalysts prepared by PV method: (- - -) 0.8 M $(NH_4)_2Cr_2O_7$, (— -) 1.7 M CrO_3, (——) 1.8 M $Cr(NO_3)_3$.

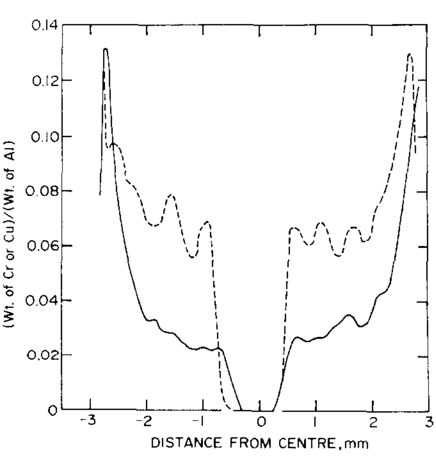

FIG. 2. Concentration profiles for catalysts prepared by PV method: (- - -) 1.8 M $Cr(NO_3)_3$, (——) 1.6 M $Cu(NO_3)_2$.

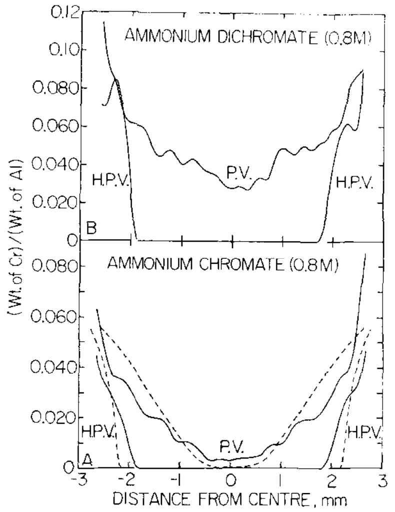

FIG. 3. Concentration curves for ammonium chromate and dichromate: (A) 0.8 *M* $(NH_4)_2CrO_4$, (——) experimental; (— —) calculated. (B) 0.8 *M* $(NH_4)_2Cr_2O_7$, experimental curves.

dried at 110°C for 8 hr and calcined at 500°C for 4 hr. XS samples were immersed in the solution for 9 days before drying and calcining at the conditions just described.

Reagent-grade chemicals were used. The solution of $Cu(NH_3)_4(NO_3)_2$ was prepared by adding concentrated aqueous NH_3 to copper II nitrate solution to give concentrations of 0.3 *M* Cu and 15 *M* aqueous NH_3.

Particles were sectioned to reveal their cross section by usual metallurgical methods as described previously (*5*). Flat specimens on a scale (μm) are required for satisfactory probe analyses; apparently pores the order of 100 Å are not detrimental. The polished surfaces seemed flat, except for a number of holes varying size up to 0.4 mm, some of which seemed to be present in the original alumina. An Acton electron probe microanalyzer with 3 spectrometers at fixed take off angles of 18° was used. The acceleration voltage of the electron beam was 15 kV. Point counting was performed at 52-μm intervals along the diameter of the circular cross section. X-Rays of Cr and Al or Cu and Al were measured simultaneously. Correction and calibration procedures have been described (*1*, *5*). Concentrations are expressed as weight ratios of Cr or Cu to Al, because the concentration of Al should remain constant.

The concentration profiles contained some widely scattered points that were eliminated by a smoothing (mathematical) procedure (*5*, *9*), and the smoothed curves are presented in the figures. From the smoothed curves the weight of metal present was calculated; this value is compared with the weight introduced in Table 1. The differences are usually less than 10%.

Adsorption isotherms for aqueous solutions of ammonium chromate and ammonium dichromate were determined by adding a known concentration and amount of solution to a known weight of finely crushed alumina spheres in closed flasks. The heat-treated and dry alumina spheres were crushed and sieved to 30–50 mesh for these

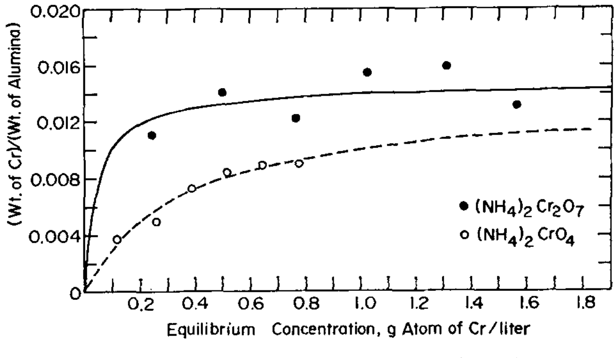

FIG. 4. Adsorption isotherms for aqueous solutions of ammonium chromate and dichromate on Kaiser alumina at 25°C.

experiments, and 20 ml of solution were added to about 1.5 g alumina in weighing bottles. Several concentrations of each solution were used. During the 30-day equilibration period, the system was stirred occasionally. The concentrations of the original and final solutions were determined by titrating with iron II sulfate using sodium *p*-diphenlyamine sulfonate as an indicator.

Viscosities of 1.8 *M* solutions of chromium III nitrate, and copper II nitrate chromic acid were measured with a Ubbelohde viscosimeter at 25°C using water as a standard. The viscosities were (cP): 1.8 *M* chromic acid, 1.04; 1.8 *M* chromium III nitrate, 3.66; 1.8 *M* copper II nitrate, 2.01.

EXPERIMENTAL RESULTS

Electron probe results are presented for catalyst particles sectioned at the center of the porous alumina sphere. Concentration profiles were determined along the diameter of the circular cross section and are presented as weight of metal per weight of Al after a smoothing (mathematical) procedure to eliminate a few widely scattered points presumably resulting from roughness of the polished surface.

Figure 1 presents chromium concentration profiles for alumina spheres impregnated by the PV method, with aqueous solutions of different chromium compounds of about the same concentration. Figure 2 compares concentration profiles for alumina spheres impregnated by the PV method with solutions of copper II and chromium III nitrates. From Fig. 1, it may be inferred that chromium III nitrate is more strongly adsorbed than chromic acid or ammonium dichromate. Similarly from Fig. 2 chromium III nitrate is more strongly adsorbed than copper II nitrate, but neither cation penetrated to the center of the particle.

Figure 3 gives concentration profiles for preparations from ammonium chromate and dichromate solutions by the PV and HPV methods. As noted earlier (*5*) for the HPV impregnations, the chromium was confined to the outer portions of the particle, but the chromium penetrated in the impregnation, drying and calcining steps, to a greater depth than that corresponding to half of the volume of the sphere. Neither the chromate or dichromate were strongly adsorbed as chromium was found in the center of the catalyst in both cases for preparations by the PV method.

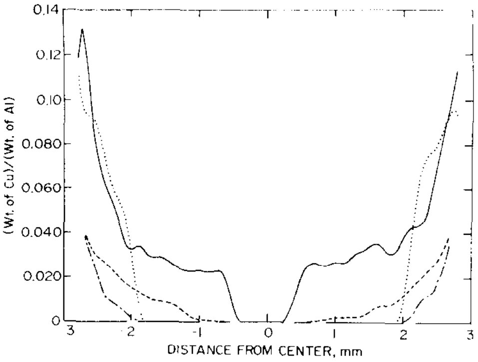

FIG. 5. Concentration profiles for copper salts: 1.6 *M* $Cr(NO_3)_2$, PV (—), HPV (····); 0.3 *M* $Cr(NH_3)_4(NO_3)_2$, PV (– – –), HPV (— –).

Figure 4 presents adsorption isotherms for chromium from aqueous solutions of ammonium chromate and dichromate at 25°C obtained by determining the concentration of the solutions after 30 days on samples of finely crushed alumina. Both chromates seem to be adsorbed moderately strongly, but the saturation values are less than half of the average concentrations of chromium in the particles of Fig. 3. Note that the chromium concentration of the dichromate solution was twice that of the chromate in the samples described in Fig. 3.

In our impregnation procedure, the solution is drawn into the particle by capillary action and concurrently the solute adsorbs on the pore walls. Events occurring during drying and calcination steps are more complicated, and the solute may redistribute. For example, evaporation of water at the periphery of the particles could "pump" the solution out of the particle and lead to large concentrations of solute at outside of the particle or the solute could penetrate deeper into the sphere in these steps. For the data of Fig. 3 this "pumping out" effect was not important as the largest concentrations of chromium were about equal to the sum of the Cr adsorbed and the Cr in the solution in the pores at the concentration of the fresh solution for the PV preparations. For HPV samples the largest concentration of Cr was always smaller than this sum. This fact and the concentration profiles suggest that the solute penetrates more than half of the pore volume, either initially or during drying and calcining.

For the PV preparations of Fig. 3, the general features of the concentration profiles may be approximated by assuming that the solution maintains adsorption equilibrium with the alumina as the solution penetrates the particle and that the solute does not move during drying. The curve for ammonium chromate is plotted in Fig. 3A. In calculating the profile the sphere was divided into 50 concentric shells of constant thickness. The alumina in the outer shell equilibrates with the entire volume of solution. The volume of solution remaining after filling the first shell at the equilibrium concentration of the first shell then equilibrates with the alumina in the second shell, etc. The average concentration of each shell is the sum of the amounts adsorbed and in the pore solution. Calculations of this type for HPV preparations (Fig. 3A) are not appropriate because the calculated profile stops when half of the pore volume is filled.

Figure 5 compares concentration profiles for PV and HPV impregnations with 1.6 *M* copper II nitrate and 0.3 *M* $Cu(NH_3)_4(NO_3)_2$ solutions. For the HPV sample the copper penetrated about 34% to the center compared with 31% for the ammonium chromate. These values correspond to penetration into 71 and 67% of the volume. For the PV method the profile for copper II nitrate was similar to the curve for chromium III nitrate, but the shoulder occurred at lower concentrations.

Finally, we note that in Fig. 2, the volume of the particles containing no chromium or copper is less than 1% of their total volume.

Profiles for PV samples of 0.3 *M* $Cu(NH_3)_4(NO_3)_2$ were similar to curves for 0.4 *M* CrO_3 in Fig. 4 of Ref. (*5*), except that this copper solution penetrates deeper than the solution of CrO_3. We infer that the copper ammine ions in a concentrated NH_3 solution are less strongly adsorbed than chromic acid.

DISCUSSION

From the shape of the concentration profiles given in this and the previous paper (*5*) we infer that the adsorption from aqueous solutions on alumina decreases in the following order: chromium III nitrate > copper II nitrate > chromic acid > ammonium dichromate > ammonium chromate. $Cu(NH_3)_4(NO_3)_2$ in concentrated NH_3 was weakly adsorbed, perhaps similar to the ammonium chromates. The strength and amount of adsorption of the solute on alumina is important in determining the nature of the concentration profile. Nevertheless, for the present chromium and copper catalysts containing 1 to 20 wt% of metal, an appreciable fraction of active material found in the catalyst was initially present in solution in the pore. For example, for a catalyst prepared from ammonium dichromate (Fig. 3) about 65% of the chromium was initially in solution in the pores. For catalysts containing 0.05–0.5 wt% active component on alumina, such as platinum group metals, adsorption on the support is the primary factor determining concentration profiles (*7*).

The present and previous (*5*) papers described catalysts prepared by impregnating alumina with a volume of solution equal to the pore volume (PV) or half of the pore volume (HPV) with drying and calcining immediately after impregnation. Another type of catalyst (XS) was prepared by immersing the alumina sphere in 20 ml of

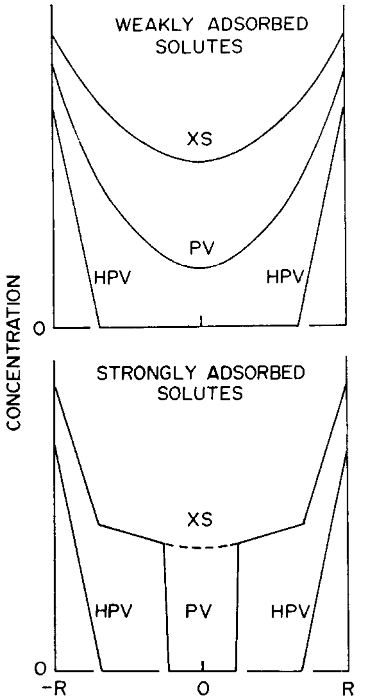

FIG. 6. Schematic representation of concentration profiles.

solution for 9 days before drying and calcining (*5*). Figure 6 summarizes in a schematic way the types of profiles found. For the PV method with a weakly adsorbed solute the concentration decreases gradually from the periphery to the center. For strongly adsorbed solutes the concentration profile decreases sharply from the outside followed by a portion of significantly lower slope and finally an abrupt drop to zero concentration. For the HPV method with both types of solutes, the solute penetrates more than half of the pore volume, and the concentration at the periphery of the particles is smaller in HPV than in PV preparations. For a weakly adsorbed solute (chromic acid) the XS method increases the concentration compared with the PV method by a substantial amount at the center of the particle and by a smaller amount of the periphery. For a strongly adsorbed solute (chromium III nitrate) the XS method increases the concentration in the outer portion only slightly compared with the PV method, but the solute is introduced to the central portion by the XS procedure. As noted earlier, this central portion is less than 1% of the total volume. For chromic acid the XS procedure introduced nearly twice as much Cr as the PV method, while for chromium III nitrate XS introduced only 10–25% more Cr than PV (Table 1).

The only difference between the XS and PV methods is the 9-day soaking in a large excess of solution for XS. In this period the solute is transported by diffusion into the particle that is filled with solution. Chromium III nitrate must diffuse very much more slowly than chromic acid, which is consistent with the viscosity of the solution of chromium nitrate being about 4 times that of chromic acid. The diffusivity of ions of chromium in these solutions should vary approximately inversely with viscosity. In the pores of the catalyst the size of the hydrated ions and the thickness of adsorbed layer may decrease diffusivity in the nitrate solution with respect to the chromic acid solution by a larger amount than the ratios of viscosities.

With ammonium chromates withdrawal of the solution from the sphere during drying and calcining was unimportant, and this result seems generally applicable to all of the present catalysts.

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