Hydrogen–Water Deuterium Exchange over Nickel–Chromia Supported on Alumina[1]

I. Catalyst Preparation and Characterization

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In this study of catalysts for the deuterium exchange reaction between hydrogen and water, nickel–chromia supported on γ-alumina spheres was the catalyst studied. Porous γ-alumina spheres were impregnated with solutions of nickel and chromium compounds. Electron probe microanalysis was used to measure concentration profiles and total nickel and chromium content. Scanning electron microscopy was used to examine the surface morphology, and mercury porosimetry was used to measure pore volumes. Total surface areas were measured by nitrogen adsorption.

Nickel from the sulfate deposited near the outside of the spheres, whereas nickel from nitrate and chloride solutions penetrated to the interior. Reducing the time of impregnation or using a wet support hindered the nickel penetration. Chromium from the nitrate and from chromic acid of low concentration was deposited near the outside of the support. If two impregnations were used consecutively, the solute from the first impregnation could redissolve and and be carried towards the center of the particle during the second impregnation. This movement could be prevented by drying and calcining after the first impregnation. Catalysts impregnated with nickelous nitrate or chromic nitrate had higher pore volumes, surface areas and pore diameters than did the support. On the other hand, the catalyst impregnated with nickelous sulfate had a lower surface area than the support.

INTRODUCTION

Nickel promoted with chromia is an effective catalyst for the deuterium exchange reaction between hydrogen and water (1,2). Nickel is considered to be the active material while chromia is both a structural and chemical promoter (2–5), that is, it creates more nickel surface area, and at the same time gives a higher rate per unit surface area.

In general, the optimum chromia content in these coprecipitated catalysts is about 15%. Both chemical and structural promotion effects increase the reaction rate up to

approximately this level, and at higher chromia contents, the rates decrease because the nickel surface area is decreased.

The study was made of hydrogen–water deuterium exchange over nickel–chromia supported on γ-alumina spheres, since it was hoped that on γ-alumina, a high nickel surface area could be obtained regardless of the amount of chromia present. The work also included a study of the metal distribution in these supported catalysts obtained by various impregnating techniques. The hydrogen-water isotopic exchange reactions on these catalysts are described in a separate report (11).

For large catalyst particles, the decrease in the concentration of reactants inwards

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from the pore mouth gives lower rates in the center of the particles compared with the external portions. Therefore, it is usually desirable to deposit the active metal near the outside of the support. Changes in the impregnating technique cause different dispersions of metals on the support, as has previously been demonstrated for impregnated chromium and copper on alumina catalysts (6–9). In this work, the dispersion of nickel and chromium on γ-alumina was studied using different salts and different impregnating times on dry as well as wet supports to assess the importance of these variables on the metal dispersion. The effect of simultaneous or consecutive impregnation with two solutes was studied as well as the effect of drying and calcining between consecutive treatments. Changes in surface morphology, surface area, and pore geometry due to impregnation, were also studied.

EXPERIMENTAL METHODS

Materials

The γ-alumina spheres were furnished by Air Products and Chemicals, Inc. The spheres selected had diameters in the range 5.5 ± 0.5 mm. Before impregnation, the spheres were heat treated at 600°C for 20 hr and stored in a desiccator until used. After heat treatment, the surface area of the support was 143 m²/g as determined by nitrogen adsorption at 77 K and the pore volume was 0.70 cm³/g as determined by the amount of water absorbed.

Impregnation of Catalysts

Alumina spheres were weighed and placed on glass plates. Open-end glass tubes with inside diameters slightly larger than the diameters of the spheres were placed over each sphere and stood upright on a glass plate. A hypodermic syringe was used to deliver an amount of solution equal to the pore volume of the particle

onto the particle. The solution covered the particle completely and was absorbed uniformly. The time required for the solution to be completely absorbed was about 8 min; this was used as the standard length of time for impregnation.

Aqueous solutions of $Ni(NO_3)_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $NiSO_4 \cdot 6H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$ and CrO_3 were prepared. The pH values of the nickel solutions were 1.49, 5.41, and 4.45 for the nitrate, chloride and sulfate, respectively. The solutions contained either just the nickel compound or both nickel and chromium compounds. Usually, the dry alumina support was immersed in an excess of solution for 8 min but occasionally it was immersed for only 3 min to limit the amount of penetrating solution. When consecutive impregnations were done, the first impregnation was for 3 min, followed by either drying or drying and calcining, and the second impregnation was for 8 min. Sometimes alumina particles were first soaked in boiling water to fill the pores with water and this was followed by immersion in an impregnating solution. After impregnation, the catalyst was dried at 110°C for 16 hr and calcined in air at 400°C for 6 hr.

Characterization of Catalysts

The catalyst spheres were imbedded in Lucite and standard metallurgical techniques (9) were used to polish off half of the sphere to reveal the cross section. The sample was polished with 6 μm diamond paste, cleaned thoroughly with alcohol, and coated with evaporated carbon for electron microprobe analysis (6–9).

Point-counting of aluminum, nickel, and chromium X-ray intensities was performed along the diameter of the circular cross section at 43 μm intervals. After correction of X-ray intensities for atomic number effect, absorption of X-rays, and fluorescence, the weight ratio of nickel to aluminum or chromium to aluminum was found as a function of particle radius. The con-

centration data were smoothed 4 times with a 7-point third degree polynominal (*10*) and the smoothed values were plotted as a function of the particle radius.

Numerical integration of the concentration curves using Simpson's rule gave the nickel or chromium content relative to aluminum. The nickel and chromium content of a catalyst determined by atomic absorption spectroscopy agreed with that from the electron microphobe analysis to within 3.5% for nickel and 13.9% for chromium. Therefore, the determination of nickel or chromium content in a catalyst with probe analysis was considered reliable.

Scanning electron micrographs were taken on broken unpolished sections of a catalyst with a Cambridge Stereoscan Mark II Instrument. The samples were coated with gold to provide electric conductivity.

A Micromeritics Model 900 mercury porosimeter was used to determine the pore radius and pore volume of the alumina support and of the impregnated catalysts. BET surface areas were determined by nitrogen adsorption at 77 K using a Perkin-Elmer Sorptometer 212D.

RESULTS

Concentration Profiles

Figure 1 shows the Ni concentration profiles on three spheres impregnated with nickelous nitrate (1.43 mol/liter), nickelous sulfate (1.47 mol/liter) and nickelous chloride (1.43 mol/liter), respectively. In each case, the dry support was immersed in an excess amount of solution for 8 min, the average time required for an amount of solution equivalent to the pore volume to be absorbed completely. Immersions for less than 8 min resulted in less nickel being absorbed. As the solution penetrated the support by capillary forces, part of the solute adsorbed on the pore walls and the concentration of solute decreased. Nickelous sulfate appeared to be strongly ad-
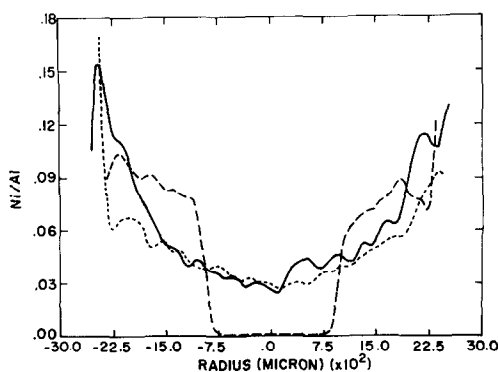

FIG. 1. Dispersion of nickel on support as a function of nickelous compound used: (—) nickelous nitrate (1.43 *M*); (—–) nickelous sulfate (1.47 *M*); (---) nickelous chloride (1.43 *M*).

sorbed by alumina. The central portion of the support contained no nickel, indicating that all the solute was adsorbed on alumina before the solution reached the center of the sphere. Nickelous nitrate and nickelous chloride were weakly adsorbed by alumina since nickel was found throughout the entire support in both cases. When equal concentrations were used, both these salts gave essentially the same nickel profiles. Since the pH of the sulfate solution was intermediate between that of the nitrate and the chloride, pH effects are not considered responsible for the strong adsorption of nickelous sulfate. Nickel contents are listed in Table 1 which includes an index to the concentration profiles reported in Figs. 1 to 5 and also includes the code numbers for these catalysts used in the exchange reaction studies (*11*).

If the alumina was immersed in boiling water for 20 min, and subsequently immersed in 1.45 mol/liter nickelous nitrate for 10 min, nickel was excluded from the core. When immersion in boiling water was followed by immersion times of 20 min or more in nickelous nitrate, more nickel was found in the interior, the nickel content being roughly proportional to the immersion time in the nickelous nitrate. Boiling water had filled the pores before

Catalyst No. [Ref. (11)]	Figure No.	Type of curve	Nickel (g/g Al$_2$O$_3$)	Chromium (g/g Al$_2$O$_3$)
543	1	—	0.0476	0
575	1	--	0.0417	0
544	1	---	0.0312	0
542	2	—	0.0240	
542	2	--		0.0062
572	2	—	0.0137	
578-U	3	—	0.0346	
578-U	3	--		0.0025
578-V	4	—	0.0492	
578-V	4	--		0.0051
578-W	5	—	0.0518	
578-W	5	--		0.0046

impregnation so that solute could only diffuse in slowly during impregnation.

Figure 2 shows the nickel and chromium concentration profiles in a sphere impregnated with a solution containing 0.15 mol/liter chromic nitrate and 0.71 mol/liter nickelous nitrate. Chromic nitrate was strongly adsorbed by the alumina (9) so all the chromium was adsorbed in an external shell of the sphere. On the other hand, nickel was found throughout the entire volume, but the shape of the nickel curve was different from that when a sphere was impregnated with a solution containing nickelous nitrate only, i.e., the solid curve in Fig. 1. Adsorption of chromia near the
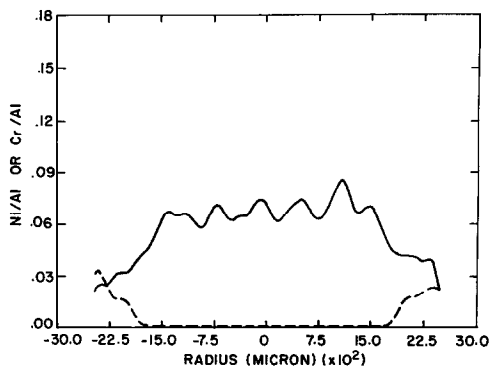

FIG. 2. The support impregnated for 8 min with a solution 0.15 mol/liter of chromic nitrate and 0.71 mol/liter of nickelous nitrate: (—-) Cr/Al; (—) Ni/Al.

exterior reduced the nickel adsorption in this region. If the spheres were immersed in boiling water for 20 min prior to impregnation, water in the pores hindred penetration of solution into the spheres and both the nickel and chromium contents were lower.

Where consecutive impregnations were performed with a chromic nitrate impregnation following a nickelous nitrate impregnation on an alumina sphere, the chromium profiles were similar, whereas the nickel profiles differed. Drying and calcining after impregnation ensured that nickelous salt would not be redissolved by the second impregnation. When the sphere was merely dried after the first impregnation, the nickelous salt was dissolved and redistributed by the chromic solution during the second impregnation, resulting in a more uniform nickel profile.

Where the sphere was impregnated with 0.3 mol/liter chromic nitrate solution for 8 min to allow the solution to fill the pores, followed by impregnation with 1.43 mol/liter nickelous nitrate solution for 3 min to limit the amount of solution penetrating the sphere, drying and calcining after the first impregnation, or merely drying, after the first impregnation, resulted in similar concentration profiles indicating that chromium was strongly adsorbed by alumina and was not redissolved by a second impregnation with nickelous nitrate solution even if the catalyst was not calcined. The nickel uptakes in both particles were 0.0496 g/g when the sphere was calcined after chromium impregnation and 0.0393 g/g when it was just dried at that stage. Calcining the particle gave a higher nickel concentration in the interior. In both cases the nickel content was somewhat higher than the 0.0305 g/g obtained when fresh alumina was impregnated for 3 min. Obviously, the first impregnations with chromic nitrate solution followed by drying only, or drying and calcining, modified the pore geometry and made the pene-
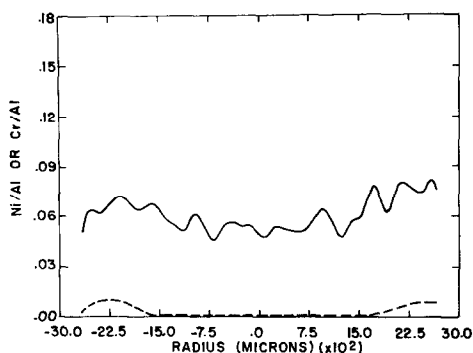
FIG. 3. The support impregnated for 10 min with a solution containing 0.08 mol/liter chromic acid and 1.51 mol/liter nickelous nitrate: (—-) Cr/Al; (—) Ni/Al.
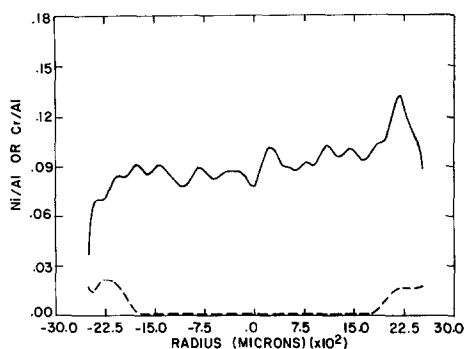

FIG. 4. The support impregnated with 1.51 mol/liter nickelous nitrate solution for 10 min, dried, calcined and subsequently impregnated with 0.08 mol/liter chromic acid solution for 10 min: (—-) Cr/Al; (—) Ni/Al.

tration of nickelous nitrate solution easier than on virgin alumina.

When impregnations were done for 3 min only, the nickel profiles differed depending on whether nickelous nitrate or chromic nitrate was impregnated and calcined first. The center of the sphere remained free of nickel when the nickel treatment came first, whereas prior treatment with chromium aided penetration of nickel to the center as noted above. However, no difference was found between the nickel profiles and chromium profiles when there was no calcining after the first impregnation.

Figure 3 shows nickel and chromium profiles on a sphere impregnated for 10 min with a solution containing 0.08 mol/liter chromic acid and 1.51 mol/liter nickelous nitrate. Chromium was found only near the outside of the sphere. The nickel profile was fairly uniform across the sphere although the nickel content near the outside was slightly higher than that near the center. It should be recalled that when chromic nitrate was used the nickel content was higher at the center (Fig. 2). Figure 4 shows concentration profiles for a support which was impregnated with 1.51 mol/liter nickelous nitrate solution for 10 min, dried, calcined and subsequently impregnated with 0.08 mol/liter chromic acid,

while the support represented by Fig. 5 was first impregnated with 0.08 mol/liter chromic acid for 10 min, dried, calcined, and impregnated with 1.51 mol/liter nickelous nitrate solution for 10 min. Chromium was found in the external shell of the sphere and nickel was found throughout the entire volume for all the impregnations using chromic acid. Different procedures for impregnation gave insignificant differences in nickel and chromium profiles. Table 1 shows the nickel and chromium contents obtained by numerical integration with the concentration profiles shown above.
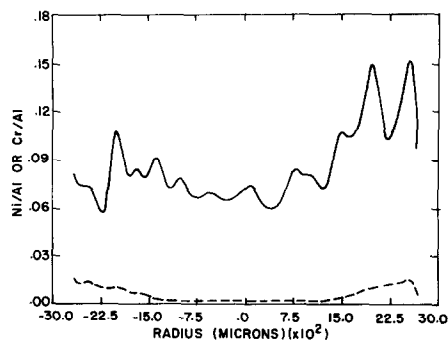

FIG. 5. The support impregnated with 0.08 mol/liter chromic acid solution for 10 minutes, dried, calcined and subsequently impregnated with 1.5 mol/liter nickelous nitrate solution for 10 min: (—-) Cr/Al; (—) Ni/Al.
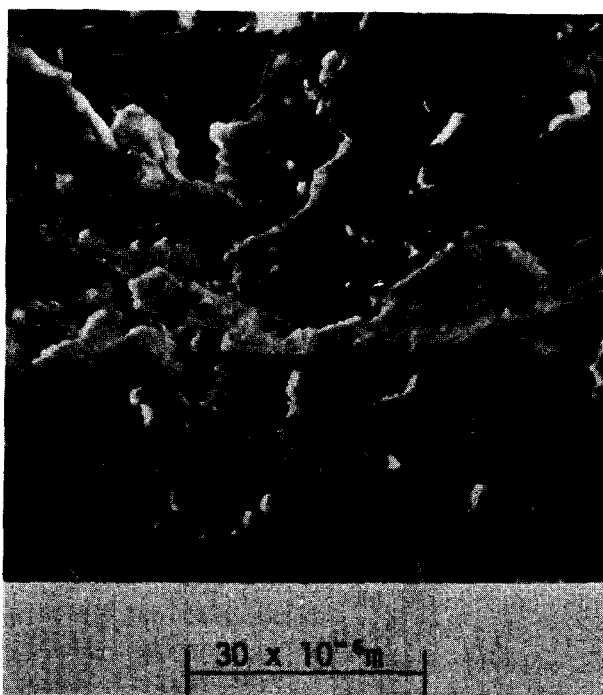
FIG. 6. Scanning electron micrograph of γ-alumina support.

Scanning Electron Micrographs

Figure 6 is a scanning electron micro-graph of an unpolished section of broken alumina support. Alumina aggregates of various sizes ranging between about 1 and 20 μm are observed. Most of the surface area and fine pores are contained within these aggregates. The spaces between the aggregates constitute macropores.

Figures 7 and 8 are micrographs of dif-ferent portions of a sphere impregnated with a solution containing 0.15 mol/liter chromic nitrate and 0.71 mol/liter nick-elous nitrate. The nickel and chromium concentration profiles on this support were shown in Fig. 2. Figure 7 shows the cen-tral portion containing only nickel and Fig. 8 shows the external portion containing both nickel and chromium. A comparison of Figs. 6 and 7 indicates that a large por-tion of the nickelous nitrate adsorbed on the exterior surface of the alumina is present as aggregates. The structure of the substrate was not modified significantly,

but chromic nitrate tended to modify the nickelous nitrate structure to a significant degree as shown in Fig. 8.

Mercury Porosimetry

Figure 9 shows the cumulative penetra-tion volume by mercury as a function of pressure, and therefore of pore diameter, determined with a mercury porosimeter. Curves are shown for a γ-alumina support, a support impregnated with chromic ni-trate solution, and a support impregnated with nickelous nitrate solution. For the alumina impregnated with chromic nitrate, the sample was taken only from the ex-ternal shell of the sphere since we were not able to impregnate a sphere uniformly with chromium. The other curves refer to whole spheres. Each curve in Fig. 9 con-tains two steep increases in pore volume corresponding to two ranges of pore sizes: micro- and macropores.

For the alumina support, the pore vol-ume determined by mercury porosimetry
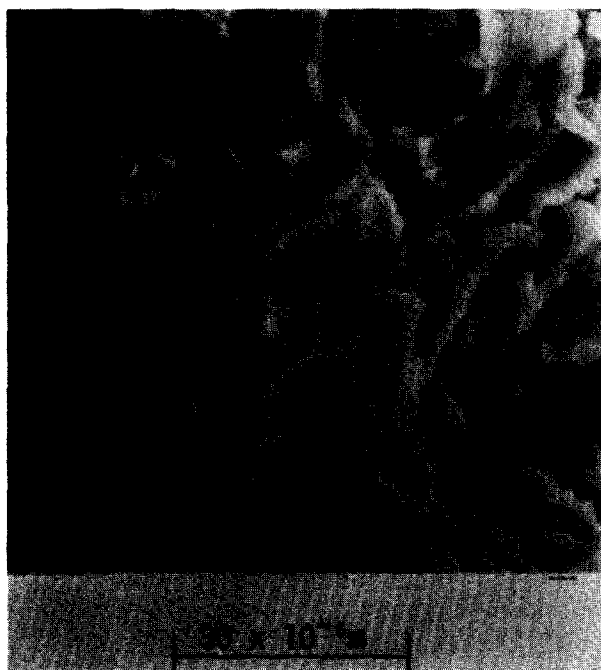
FIG. 7. Scanning electron micrograph of γ-alumina impregnated with nickelous nitrate.
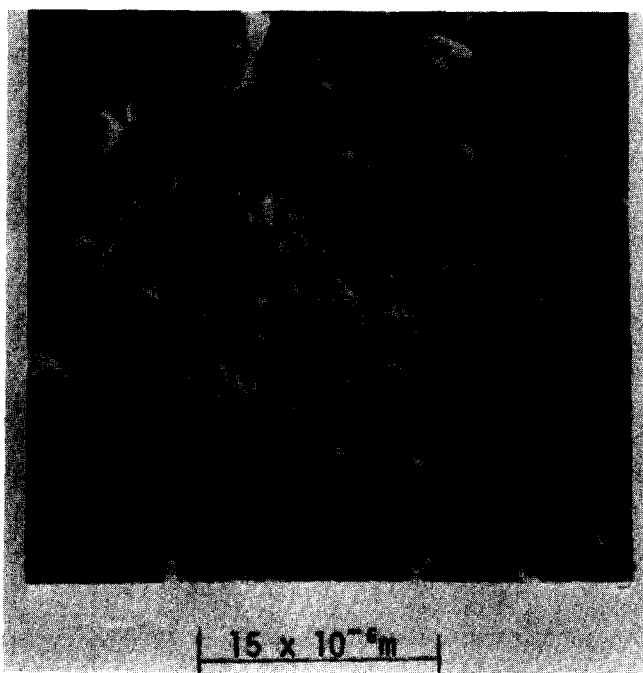

FIG. 8. Scanning electron micrograph of γ-alumina impregnated with nickelous nitrate and chromic nitrate.
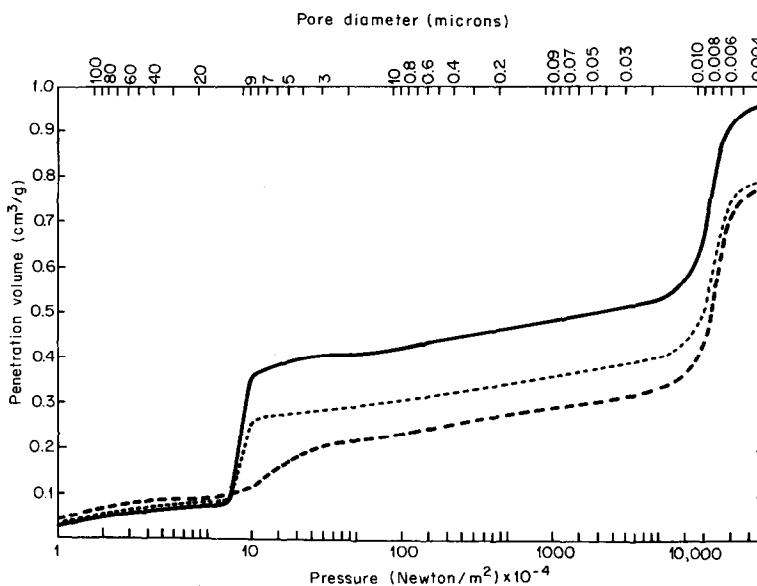
Pore diameter (microns)

FIG. 9. Accumulative penetration volume by mercury as a function of pore diameter on support and catalysts: (—) alumina impregnated with $Cr(NO_3)_3 \cdot 9H_2O$; (--) alumina support; (---) alumina impregnated with $Ni(NO_3)_2 \cdot 6H_2O$.

was 0.73 cm³/g compared with 0.70 cm³/g determined from the amount of water absorbed. The most frequent pore diameters were 7 nm and 6 μm. For alumina impregnated with chromic nitrate solution, the pore volume was 0.93 cm³/g with pore diameters of 8 nm and 10 μm. For the alumina impregnated with nickelous nitrate solution, the pore volume was 0.76 cm³/g and the most frequent pore diameters are 7.3 nm and 10 μm. Thus both the pore volume and pore size were increased by impregnation with nickelous nitrate or chromic nitrate, drying and calcining. The increase was greater for the impregnation with chromic nitrate than with nickelous nitrate.

Nitrogen Physisorption

The BET surface areas of the spheres determined by nitrogen physisorption at 77 K are shown in Table 2. The error limits shown are the experimental reproducibility for six samples. The sphere impregnated with nickelous nitrate solution had nickel distributed across the entire sphere and

has a surface area 14% higher than the support. The sphere impregnated with chromic nitrate solution had chromium only in an external shell and a sample taken from the external shell had a surface area 44% higher than the support. The sphere impregnated with a solution con-

TABLE 2
BET SURFACE AREAS OF SUPPORT
AND CATALYSTS

Sample	BET surface area (m²/g)
Alumina	143 ± 5
Support impregnated with nickelous nitrate	163 ± 5
Support impregnated with chromic nitrate[a]	206 ± 6
Support impregnated with a solution containing both nickelous nitrate and chromic nitrate	141 ± 5
Support impregnated with nickelous sulfate[b]	132 ± 4

[a] Sample taken from external shell of particle containing Cr.

[b] Sample taken from external shell of particle containing Ni.

taining both nickelous nitrate and chromic nitrate had chromium only in an external shell and the nickel content in the external shell was lower than in the central core. The surface area of this sphere was about the same as for untreated spheres. However, the sphere impregnated with nickelous sulfate solution had a slightly lower surface area than the original alumina.

The increase in surface area after impregnation with nickelous nitrate or chromic nitrate alone may be due to the formation of porous species on the alumina. Impregnation with a solution containing both nitrates caused an increase in surface area in the central core which contained only nickel and a decrease in surface area in the external shell which contained nickel and chromium. The net result was no overall change in surface area. Possibly impregnation with nickelous sulfate blocked some of the fine pores in the external shell and caused a decrease in surface area there.

DISCUSSION

The alumina used consisted of porous aggregates of various sizes between about 1 and 20 μm. The spaces between the aggregates are very large pores and most of the surface area and the fine pores are within the alumina aggregates. The average radius of the fine pores by mercury porosimetry is 3.5 nm. The hydrated radii of Ni^{2+}, Cr^{3+} and CrO_4^{2-} are 0.404 nm, 0.461 nm and 0.375 nm, respectively (12), so these ions easily penetrate the pores of the alumina support.

Several processes were involved in the impregnation of the dry alumina. These included the penetration of solution by capillary forces, the adsorption of solute on the pore walls, and the diffusion of solute in the pore solution, as discussed in an earlier paper by Chen and Anderson (9).

If the alumina is already wet, capillary penetration of the impregnating solution is eliminated. The solute diffuses in water in the pores and adsorbs on pore walls. On drying the impregnated particle, evaporation of water near the periphery concentrates the pore solution, which causes more diffusion of solute toward the center of the particle. If the concentration of the pore solutions reaches the solubility limit, then solute precipitates on the alumina. Both the solute adsorbed on the pore walls and the solute in the pore solution contribute to the total amount of the solute which is finally deposited in the particle.

If a support is immersed in a solution for a short time, the amount of solution penetrating the support is not enough to fill the pores. For a unimodal micropore structure, the solution would not reach the center of the particle. However, for a bimodal pore structure with macro- and micropores, the solution penetrates the one set of pores preferentially leaving the other set of pores near the outside of the particle unfilled. Whether the macro- or micropores fill first will depend on the contact angle of the solution on the alumina. If the solution has a high contact angle on the solid, it will be excluded preferentially from the fine pores, but if it has a low contact angle and wets the solid well, it will be drawn into the small pores. The aqueous solutions used should have a low contact angle on alumina which has not been too drastically dehydroxylated.

As an impregnating solution containing two solutes penetrates the support, the more strongly adsorbed solute is preferentially adsorbed and deposits near the pore mouth. The more weakly adsorbed solute tends to penetrate to the center of the particle. Apparently alumina adsorbs nickelous sulfate and chromic nitrate strongly but adsorbs nickelous nitrate and chromic acid only weakly.

If two solutes are used consecutively, a weakly adsorbed solute such as nickelous nitrate can redissolve during the second impregnation and be carried toward the

center of the particle. This movement can be prevented if the particle is dried and calcined after the first impregnation. If the solute in the first impregnating solution is strongly adsorbed, it will not be redissolved by the second impregnating solution.

ACKNOWLEDGMENTS

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