

Nickel Crystallite Size and Net Activity of Hydrogenation Catalysts

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ABSTRACT AND SUMMARY

Among supported nickel-based hydrogenation catalysts, the Ni crystallite size apparently plays a secondary role in net hydrogenation activity for undistilled tallow fatty acids and nonselective hydrogenation of oxidized soybean oil. The nickel crystallite size measured by the x-ray diffraction profile broadening technique of Scherrer varied between 55 Å and 150 Å. The commercial catalyst with the smallest nickel crystallite size, in the samples studied, was not the most active for hardening soybean oil, while fatty acid hydrogenation showed a large crystallite catalyst to have the highest activity. Since the percent reduced nickel used in catalytic hydrogenation is not well known if the Ni/NiO ratio is poorly defined, relative activities were then correlated with qualitative x-ray diffraction measurements of the Ni/NiO values. Again, there was no trend in activity as a function of Ni/NiO. This apparent puzzle is probably due to real differences in the micro structure of the catalyst support. A series of experimental reductions using a common green catalyst led to very good correlations between net activity for fatty acid hydrogenation and the crystallite size and Ni/NiO ratio. On a given support, the crystallite dimension can be modified by the reduction treatment and is not sharply fixed by the selection of nickel salt and support. If the stoichiometric ratio of hydrogen is lowered, the crystallite dimension is reduced, but so is the qualitative efficiency of reduction (Ni/NiO), with the result that an exceptionally small crystallite size catalyst may be less active than one with larger crystals, but with more reduced Ni/unit weight.

INTRODUCTION

It has been shown for the hydrogenation of ethylene on nickel in a packed-bed flow reactor that catalyst particle size exerts a marked influence on observed reaction rate. Fulton and Crosser hold that the influence of particle size will be strong whenever an exothermic surface reaction is involved (1). It is intuitively to be believed not only that particle size is important in such reactions but that the size of individual Ni-crystallites is important. Particle size considerations introduce film diffusion and thickness factors into the reaction kinetics scheme, while crystallite size is expected to dominate specific reactivity if diffusion effects are not important (2).

In the hydrogenation of fatty oils the importance of film effects has long been understood at least intuitively. As far back as 1917, Moore, Richter, and Van Arsdel (3) reported that iodine values were lower for hydrogenations carried out at increasing rates of agitation. Eldib and Albright codified the role played by differing agitation schemes, and the role of process variables in fatty oil hydrogenation is generally well understood (4). Allen and Covey used polynomial regression analyses to define response surfaces that involved temperature, agitation rate, and hydrogen pressure (5).

The role of catalyst fraction or concentration has been amply investigated though the ramifications of specific

reactivity in terms of crystallite size appears to have been seldom studied. Hydrogenation of fatty oils has been, characteristically, dominated by considerations of end product nature (selectivity) and process economics. Changes in specific reactivity related to the sizes of Ni-crystallites would be of marginal economic value to catalyst users: in fact, some experiments in selectivity attainment have been aimed at the reduction of specific reactivity (6) by treatment of catalysts with H₂S and O₂.

At this laboratory we expected to obtain a clear correlation between the active metal crystallite size and hydrogenation activity of nonselective catalysts. We explored this argument with unsupported Ni in a limited way and with various commercial, supported Ni hydrogenation catalysts.

Supported Catalysts

The use of pure metal catalysts in heterogeneous, liquid phase reactions is uncommon. In some cases, finely divided pure metals or alloys have been used (7,8) but industrial catalysts are generally metals dispersed in the oxidized state on refractory supports such as clay, kieselguhr, or silica-alumina and reduced in situ. In the case of fatty acid and edible oil hydrogenation catalysts, the reduced catalyst is usually dispersed, in an absence of air, into hardened fat to stabilize it and distributed as waxy flakes or granules. Popowicz et al found a sharp correlation between the activity of Ni/Al₂O₃ catalysts and the thermal treatment of the green (unreduced material) catalyst (9). The temperature of reduction also exerted a strong effect on activity. Adamenkova and Poltorak (10) found that conditions of preparation strongly affected the activity of Pd/SiO₂ for H₂O₂ decomposition.

In the case of Ni hydrogenation catalysts, the support plays an essential role. It permits fast, high temperature reduction of green material with little compromise of activity. It permits the catalyst to retain small crystallite size by providing a real barrier to interparticle growth (sintering of actual metal). Koestler and Meisel (11) argue that the primary crystallite size of active Ni, in hydrogenation catalysts, is determined by the NiO crystallite size in the unreduced, green catalyst. Continuous and noncontinuous reduction of green material in this laboratory indicates that Koestler and Meisel's conclusion is provisionally correct. Work reported here shows that even for relatively short residence times in the hot reduction zone of a continuous processor the resultant crystallite size is modified by changes in process variables. It has been shown, too, that in an absence of support, the crystallite growth is extensive due presumably to sintering.

Some preliminary work beginning with extremely fine nickel hydrate [Ni(OH)₂] had been done initially to test the feasibility of using unsupported, dry-reduced catalysts. It was assumed that reduction at temperatures of the order 450 C would cause considerable sintering; however, the attempts were justified because an extensive, regular supply of very small crystallite (~40 Å) Ni(OH)₂ was available. It is generally accepted that given regular thermal reduction processing the number of nuclei for crystallite formation on a support is governed by the process of impregnation (12). From a reasonable model for nucleation it should be possible to derive resultant crystallite sizes for finished catalysts that conform to the order-of-magnitude of measured crystallite sizes.

By assuming that impregnation fills pores uniformly and that the drying process retains that amount of Ni salt, we can use the experimental pore volume (PV) and average

pore radius (R) to calculate an average crystallite size. If we also assume the "average pore" is $2R$ long and $2R$ wide, the number of cells to be impregnated, N_x , is $PV/2\pi R^3$ (g support)⁻¹. The catalyst from the reduction process is 100f percent Ni where f is the Ni fraction. The number of Ni-atoms/g catalyst is then derived normally, giving $n(\text{Ni}) = fN^\circ/(1-f)58.71$ where N° is Avogadro's number. The nickel atoms per cell is just

$$\eta \equiv n(\text{Ni})/N_x = f N^\circ (2\pi R^3)/(1-f)58.71 \quad (\text{I})$$

If we do the appropriate reductions and assume for diatomaceous earth clay, $PV = .50 \text{ cm}^3/\text{g}$. $R = 50 \text{ A}$, we get, for a 40% Ni catalyst $\eta = 10.7 \times 10^3$ atoms/nucleus. Assuming, for convenience, cubic form, we have cubes of ~ 22 Ni-atoms/edge. The x-ray analysed parameter for Ni is the cubic diagonal, $D(111)$, and for this calculation $D(111)$ is $\sim 45 \text{ A}$. This is in order-of-magnitude agreement with x-ray diffraction measurements of common catalysts. For a support as described, the average crystallite size $D(111)$ is shown (Fig. 1) plotted as a function of Ni-fraction (in the finished materials).

EXPERIMENTAL PROCEDURES

Commercially obtained hydrogenation catalysts from four suppliers were investigated. From the Girdler Division of Chemetron, Incorporated, (Louisville, KY) G-15, G-53, and G-70. From the Harshaw Company (Cleveland, OH), Ni-0109F, Ni-0123F, Ni-3201F, Ni-5000F, Ni-0104P, and Ni-1404P, the P and F designations referring to the form supplied (stabilized powder or fat protected). Harshaw's Ni-5000F is a wet reduced catalyst. From the PVO company of Boonton, NJ, an uncoded sample referred to as "wet-reduced." From the Konigswarter and Ebel Corporation of Hagen, W. Germany, KE/KTR and KE/NT, dry- and wet-reduced catalysts, respectively.

X-ray diffraction measurements were made using a Philips Electronics Mark II diffractometer. Copper radiation ($\lambda = 1.5405 \text{ A}$) was used, in conjunction with a curved crystal (LiF) monochromator.

Samples of fat-protected catalysts were melted into standard holders for diffraction measurements. The plane of diffraction was defined by back-filling the holders while they were clamped to glass microscope slides.

Hydrogenation experiments were done in Parr Equipment Company (Moline, IL) 2 liter converters. Fatty acid hydrogenations were done at 0.15% Ni using 1000 rpm agitation. The converter is heated under vacuum to 105 C. After attaining 105 C temperature, the system is evacuated for 10 min then heated under vacuum to 150 C. Catalyst, premixed with retained raw stock, is then washed into the converter and the converter pressurized (5 psig) with nitrogen. The bomb is pressurized to 365 psig with hydrogen which is then slowly bled off (5 min). The converter is then pressurized to 365 psig and the hydrogenation allowed to proceed. The temperature is controlled and constrained to remain below 210 C.

Edible oil hardening was done at 40 psig hydrogen pressure using 640 rpm agitation and temperature stabilization at $210 \pm 2 \text{ C}$. Vacuum was used throughout the heating process: hydrogen at the reaction pressure was purged through the soy-bean oil charge for 1-2 min at an intermediate temperature ($\sim 110 \text{ C}$). Vacuum was re-established and conversion begun 5 min after attaining the desired temperature (210 C). Until hydrogenation was begun, the catalyst was retained in a dropping chamber over the heated feedstock.

The fatty acid rawstock, undistilled, split bleachable, fancy tallow fatty acids were obtained from the Acme Hardesty Company, Inc. (New York, NY). The properties

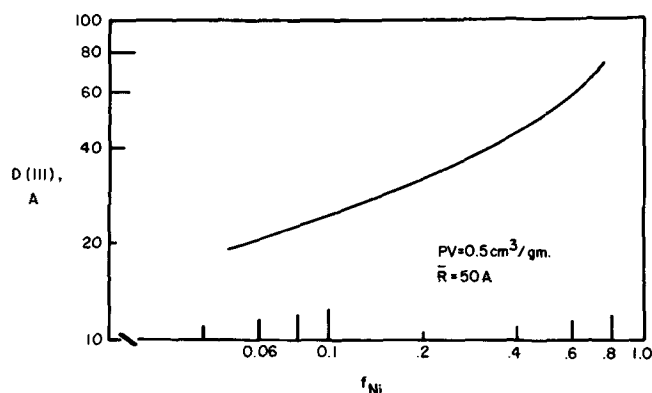


FIG. 1 Plot of crystallite size $D(111)$ for nickel supported on a substrate with $PV = 0.5 \text{ cm}^3/\text{g}$ and $R = 50 \text{ A}$.

were: Iodine Value (AOCS) 59.5; Acid Number 200.9; Peroxide Value 2.8 ME/kg; Titer 40.1 C. The oxidized soybean oil was originally obtained from the Loos and Dillworth Company of Bristol, PA. Its properties were: Iodine Value 131; Free Fatty Acids 0.08%; Saponification Value 194; Peroxide Value 42.2 ME/kg. Batch reduction of green materials, whether supported or unsupported, were done in small stainless steel bottles using zero grade gases and no agitation.

A 6 in. rotating kiln reactor was used for continuous reduction testing. The feed rate could be varied from $\sim 225 \text{ g/hr}$ to $\sim 500 \text{ g/hr}$. Rate of revolution, temperature, and tilt angle could also be varied. The entire system was flushed with H_2 and reduction carried out with regular bottled hydrogen containing small amounts of CO_2 and H_2O . A means to handle samples in a completely air-free atmosphere was used with this reactor. No materials from either reactor were exposed to air, before protecting the catalysts with melted, hard soybean oil (IV ~ 3).

RESULTS AND DISCUSSION

Crystallite Size

The method of Scherrer which assumes x-ray diffraction line profiles are Gaussian was used to determine crystallite size (13). In this scheme, the Scherrer equation for crystallite dimension perpendicular to a given hkl -direction is

$$D(hkl) = K\lambda/B \cos \theta \quad (\text{II})$$

where $D(hkl) \equiv$ dimension perpendicular to the hkl axis.

$K \equiv$ constant dependent on crystal shape

$\lambda \equiv$ wave-length of analyzing radiation

$B \equiv$ line width of the hkl diffraction line

$2\theta \equiv$ Bragg angle of hkl -line

From small crystallites ($D < 80\text{-}90 \text{ A}$) no correction to B is required. For $D > 80 \text{ A}$, the precise determination of B is complex (14), but for $D(hkl)$'s reported here, B is taken from Warren's simple correction (15).

In anticipation of fatty oil hydrogenation experiments, the Scherrer crystallite dimension of the procured catalysts was determined. They are listed in Table I, below, along with a secondary measurement of the relative intensity of the closest measurable NiO X-ray diffraction maximum.

The crystallite sizes of twelve commercial catalysts range from a small crystallite size of 44 A to a largest size of 150 A. Three of the catalysts are wet-reduced catalysts whose crystallite sizes may be expected to be quite small since they are the result of turbulent, dilute, homogeneous nucleation at reasonably low temperatures. It is noteworthy, however, that several dry-reduced catalysts had smaller sized crystallites than two of the wet-reduced

TABLE I
Crystallite Dimension and Ni/NiO for Commercial Hydrogenation Catalysts

| Catalyst | D(111),A | Ni/NiO |
|------------------------|----------|--------|
| G-15 | 150 | 5.76 |
| G-53 | 83 | 6.78 |
| G-70 | 54 | 5.36 |
| PVO ^a | 68 | 6.52 |
| Ni-5000-F ^a | 44 | 3.31 |
| Ni-3201-F | 60 | 3.85 |
| Ni-0104-P | 95 | 9.76 |
| Ni-0109-F | 112 | 13.3 |
| Ni-1404-P | 63 | 1.48 |
| Ni-0123-F | 55 | 3.12 |
| KE/KTR | 60 | 2.40 |
| KE/NT ^a | 60 | ~3 |

^aWet-reduced catalysts

materials. We also expected due to the form of the reduction process that wet-reduced catalysts would be most thoroughly converted to free Ni. Again the expected result was not realized. Using the Ni/NiO peak ratio as a qualitative measure of the Ni/NiO ratio in the finished catalyst, several dry reduced species were clearly more efficiently reduced than wet-reduced catalysts.

All the tested materials are to some degree selective catalysts but G-15, G-70 and Ni-5000F, Ni-3201F, and KE/NT are marketed as highly selective edible oil catalysts. As this data summary indicates, they show no consistent trends either in D(111)-values or Ni/NiO ratio if compared to other hydrogenation catalysts.

Catalysts in which there is a good deal of unreduced NiO require an altered means to measure the line-width of the Ni(111)-diffraction maximum. Figure 2a shows the x-ray pattern of an almost equimolar mixture of Ni and NiO. The lines are quite sharp (these are large crystallites) but the principal NiO line is very close to the principal Ni Line, the (111)-line. In the case of catalysts such as those shown in Figures 2b and d, the broadened Ni(111)-line and the NiO(200)-line interfere substantially. Figure 2b shows a catalyst containing a large fraction of NiO in a mix that is basically large crystallites of both. Figure 2c indicates a more highly reduced catalyst and the NiO(200)-line does not interfere with the measurement of the Ni(111)-line-width. Lastly, in Figure 2d we see the difficulty at its most troublesome. The NiO(200)-line is not readily distinguishable from the Ni(111)-line and a half-width measurement is impossible without making additional assumptions. For this case, the Ni(111)-line-shape is assumed centro-symmetric

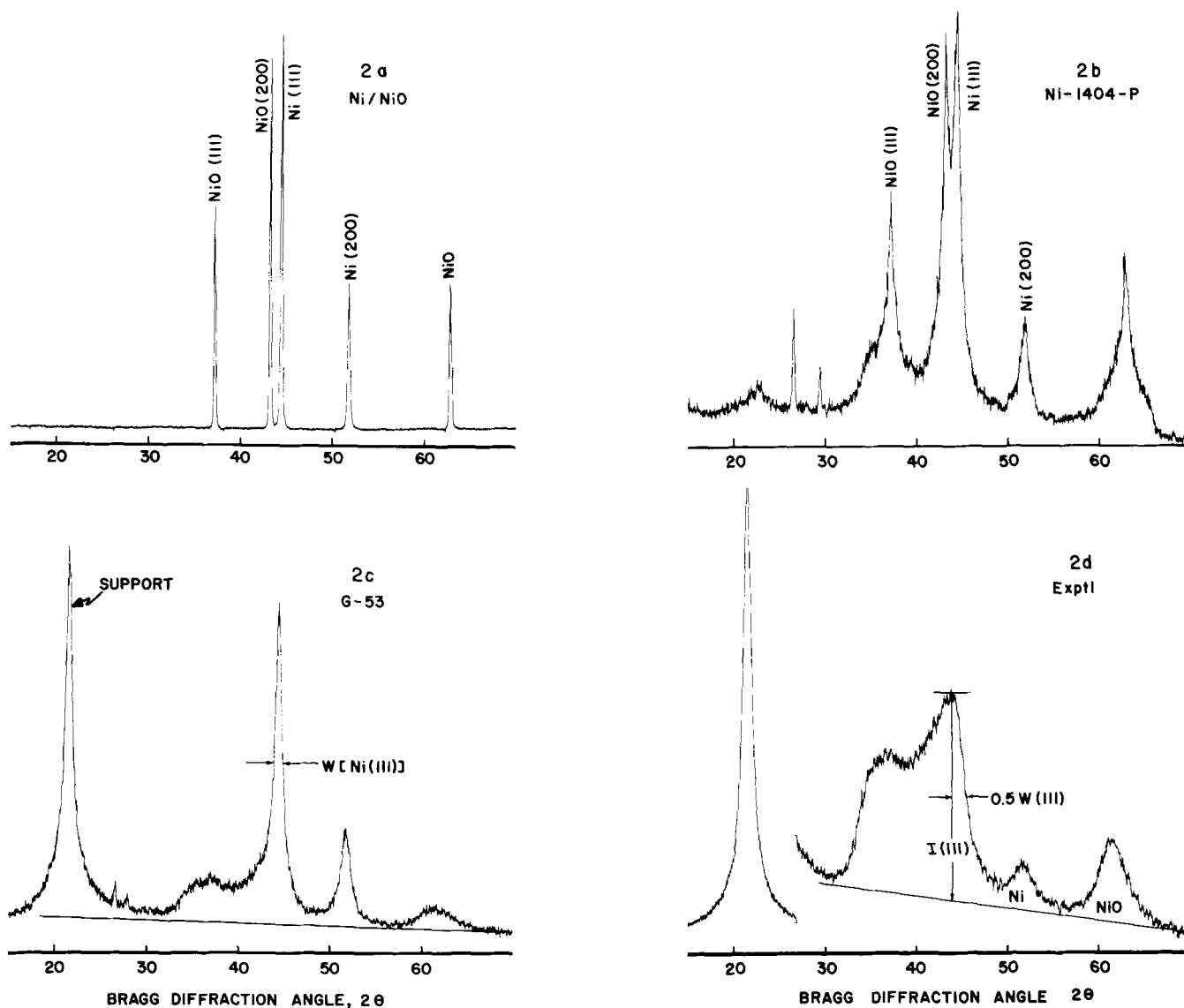


FIG. 2. X-ray diffraction profiles indicating positions of principal diffraction maxima for Ni and NiO. 2a, mixture of large crystal forms of Ni and NiO; 2b, Harshaw 1404-P; 2c, Girdler G-53; 2d, an experimental catalyst made by continuous reduction.

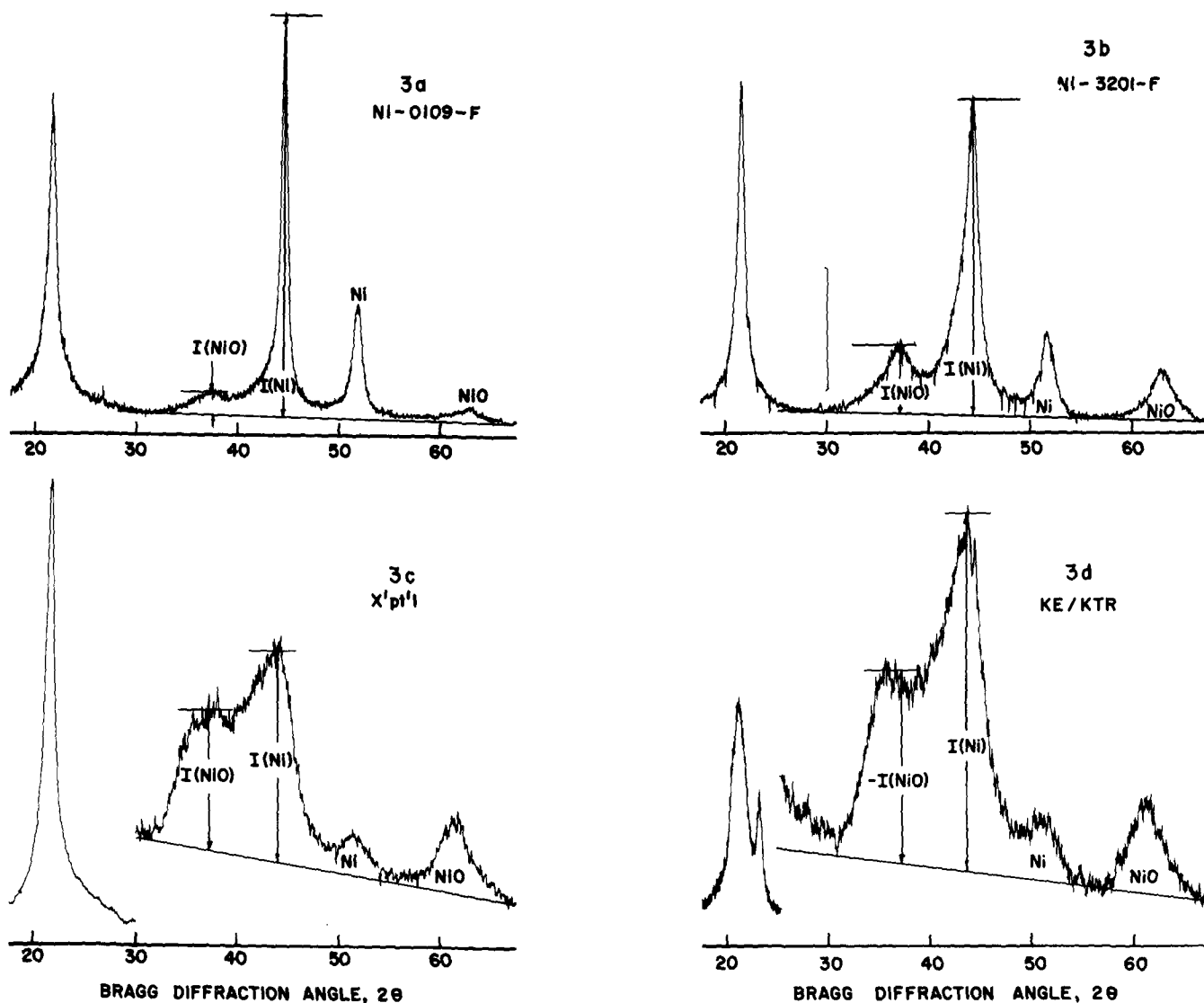


FIG. 3. X-ray diffraction profiles of catalysts indicating differences in degree of reduction of NiO. 3a, Harshaw Ni-0109-F, with Ni/NiO = 13.3; 3b, Harshaw Ni-3201-F, with Ni/NiO = 3.85; 3c, an experimental catalyst with Ni/NiO = 1.48; 3d, KE/KTR with Ni/NiO = 2.40.

and the line width is calculated from double the width of the back-side of the Ni(111) profile as shown in Figure 2d. This technique was used for all those catalysts where the x-ray diffraction maximum for the Ni(111)-line was not clearly symmetric at least to the half-height line.

Qualitative data concerning the efficiency of NiO reduction can be obtained from x-ray data. In Figures 3a-d, the x-ray diffraction spectra of three commercial catalysts are shown with specific identification of the intensities used to calculate the Ni/NiO ratio. This is the ratio of the intensities of the Ni(111) peak to the NiO(111) peak. For nickel, the (111)-line is the most intense line while for NiO, the (111)-line is the second most intense. In catalyst testing, it is rare that the Ni/NiO ratio can be calculated from the Ni(111) and the Ni(200), because one generally dominates the other.

Hydrogenation-Activity

Of all the catalysts tested for net activity using a high peroxide value soybean oil, the most active was the Girdler Chemical Company catalyst G-53. It also had exceptionally high activity for hydrogenating undistilled tallow fatty acids.

All the catalysts for which we had measured $D(111)$ -values were not tested, but from the sampling used it was clear that crystallite size did not play a dominant role, as expected, in specific activity. It was clear from limited fatty

acid hydrogenations, where agitation was more rapid and hydrogen pressure was much higher that crystallite size was no more important in this kinetics scheme than in soybean oil hydrogenation.

Using a net hydrogenation activity index already reported (16), linear regression analyses were used to define hydrogenation rate constants and all catalysts tested were compared to the reference catalyst, G-53. We then used a simple correlation to calculate a "catalyst defect fraction." The catalyst defect fraction is the ratio of the concentration of test catalyst, C_x , to the concentration of the standard catalyst, C_o , required to yield the same rate constant. If $C_x/C_o > 1$, catalyst is inferior in net activity to the reference catalyst.

In Table II below, we have listed the tested catalysts, their crystallite dimensions and the defect fraction which indicates relative activity with respect to the reference catalyst.

For hydrogenation of undistilled tallow fatty acids, the measure of activity is a simple lowering of the iodine value (IV) after a fixed period of hydrogenation. The value calculated is $[1-IV(90)/IV(0)]$ where IV(0) is the initial IV and IV(90) is the IV after 90 min of hydrogenation. These data are summarized in Table III as the Iodine Value Efficiency (IVE).

From this it appears clear that crystallite size does not, in substantial manner, control the catalytic activity of sup-

TABLE II

Summary of Activity Testing (Soybean oil), Catalyst Defect, and Crystallite Dimension

| Catalyst | D(111),A | %Ni(C _x) | Rate constant | C _o | C _o /C _x |
|-----------|----------|----------------------|---------------|----------------|--------------------------------|
| G-53 | 83 | 0.100 | -0.005298 | 0.100 | 1.00 |
| G-70 | 54 | .0284 | -0.003537 | 0.0264 | 0.93 |
| G-15 | 150 | .0575 | -0.004180 | 0.0429 | .75 |
| KT/KTR | 60 | .100 | -0.004704 | 0.0638 | .64 |
| Ni-0109-F | 112 | .076 | -0.003650 | 0.0288 | .38 |
| Ni-3201-F | 60 | .100 | -0.003862 | 0.0338 | .34 |
| Ni-0123-F | 55 | .100 | -0.003648 | 0.0288 | .29 |

TABLE III

Summary of Activity Testing (Fatty Acids) and Crystallite Dimension

| Catalyst | D(111),A | IV(90) ^a | IVE(%) ^b |
|-----------|----------|---------------------|---------------------|
| G-53 | 83 | 8.7 | 85.4 |
| KE/KTR | 60 | 9.7 | 83.6 |
| Ni-3201-F | 60 | 13.7 | 77.0 |
| Ni-5000-F | 44 | 18.5 | 68.9 |
| PVO | 68 | 17.5 | 60.5 |

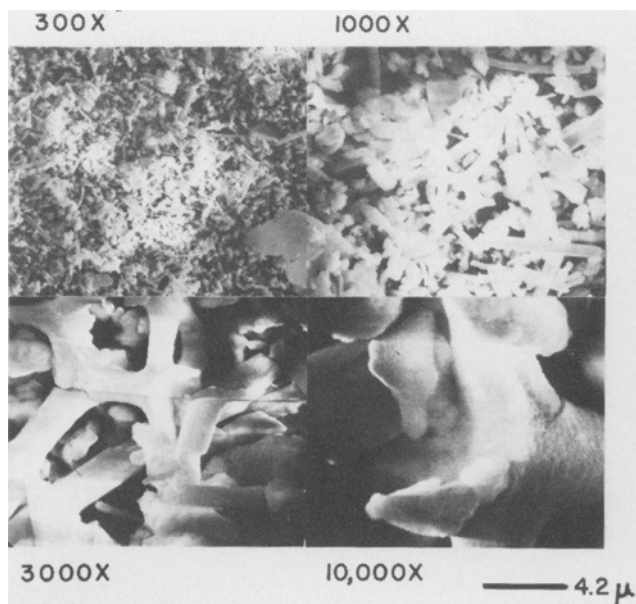
^aIV = Iodine value^bIVE = Iodine value efficiency

FIG. 4. Scanning electron micrographs of active material from Girdler G-53. The fat has been removed by extraction in hydrocarbon solvents.

ported catalysts. A study of the literature would indicate that, once a support/impregnation scheme had been selected, reduction should have little effect on the activity of the finished product.

Both these conclusions seem provisional at best. A study of the literature of hydrogenation makes clear that net (nonselective) activity should be a function of crystallite size (17,18) and despite evidence to the contrary (11), it is expected the conditions of reduction would have a strong modifying effect on crystallite size and reactivity.

The agency that can modify the role of the relative effective surface and hence the activity of Ni catalysts is the support material. Effects due to inter pore diffusion appear most likely to control the processes we measure as "net activity," and the pore structure of the support must play a very large part in determining the kinetics of reaction. The work of Ciola and Burwell (19), Freund and Hurlburt (20),

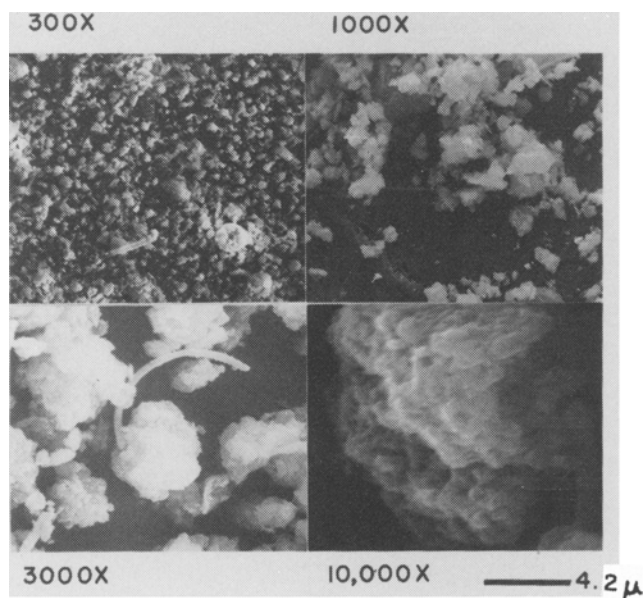


FIG. 5. Scanning electron micrographs of active material from KE/KTR.

and Watt and Wadling (21) supports this conclusion. Primary importance, therefore, rests in selection of the support substrate rather than in efficacy of the reduction process. Riesz and Weber (22) and others (23) made remarkable catalysts by using molecular sieves and natural zeolites as supports indicating conclusively the preeminence of the support in this kind of kinetics considerations.

X-ray line broadening measurements can be used to follow the process of sintering during the reduction process. In practice, however, sintering of supported Ni crystallites usually has not been a problem. For unsupported nickel, sintering can be measured this way. If the crystallite sizes of two Ni(OH)₂ samples are measured and both reduced at ~480 C, the growth of larger crystals of Ni is startling.

Two samples of Ni(OH)₂, a fine material from Shepard Chemical Co. (Cincinnati, OH) and an ESB Inc. product were x-rayed. Using the Scherrer equation, the average crystallite sizes were found to be:

1. Ni(OH)₂ 49A
2. Ni(OH)₂ >300A

Both materials were reduced in 80/20 N₂/H₂ at 480 C. The crystallite sizes of the two materials after reduction were both of the order 300 A, with the reduced fine material showing more qualitative line broadening. Neither showed hydrogenation activity until the percent Ni approached 0.4%—a very low reactivity.

If one wants to test the effects of crystallite size on total hydrogenation activity, it must be done, therefore, on a series of catalysts that use the same support structure. That the supports used in commercially supplied catalysts differ very importantly can be seen in Figures 4 and 5. These are

TABLE IV

| Iodine Efficiencies, and Crystallite Dimensions of Continuously Reduced Catalysts | | | | |
|---|-----------------------|--------------------|---------------------|---------|
| Feed Rate g/hr | H ₂ -ratio | Reduction temp, °C | IVE(%) ^a | D(111)A |
| 225 | 18.2 | 450 | 92.6 ± 1.1 | 20 |
| 225 | 18.2 | 471 | 93.2 ± 0.9 | 20 |
| 450 | 18.2 | 470 | 93.4 ± 0.9 | 30 |
| 450 | 18.2 | 453 | 93.1 ± 0.6 | 22 |
| 450 | 9.1 | 470 | 90.7 ± 1.2 | 25 |
| 450 | 9.1 | 454 | 88.8 ± 1.7 | 24 |

^aIVE = Iodine value efficiency

scanning electron micrographs of two commercial fatty acid catalysts after extraction and removal of the hardened fat. Sample A(G-53) had a BET surface area of ~30 m²/g, and B(KE/KTR) a BET surface area of ~80 m²/g. Support A particles are larger but highly "shaped" pieces compared to support B. The lower BET area of A may indicate a smaller surface for impregnation, but one that is more accessible to reactants when it is dispersed into hot, agitated oil.

A common lot of green material—a basic nickel carbonate on kieselguhr—was used to test whether the effect of crystallite size could be measured, and whether, indeed, crystallite dimension and Ni/NiO ratio as seen by x-ray dif-

TABLE V

Iodine Efficiencies and Crystallite Dimension for Catalysts Reduced with Varying H₂-Ratios (All Reductions at 450 g/hr at 470 C)

| H ₂ -ratio | IVE(%) ^a | D(111),A | Ni/NiO |
|-----------------------|---------------------|----------|--------|
| 18.2 | 93.6 | 23 | 1.44 |
| 14.6 | 92.7 | 23 | 1.34 |
| 10.9 | 92.1 | 21 | 1.19 |
| 9.1 | 89.4 | 17 | 1.19 |

^aIVE = Iodine value efficiency

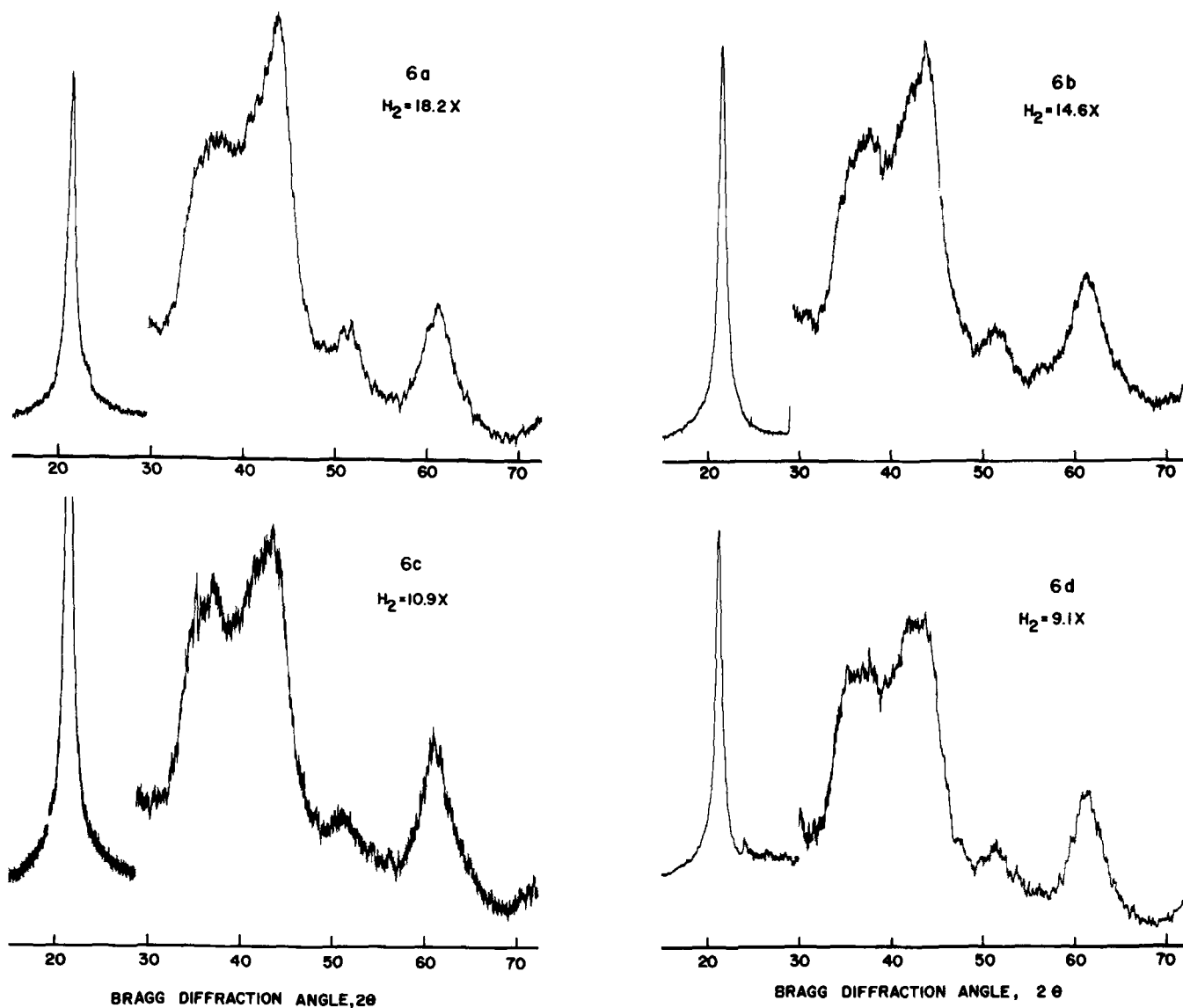


FIG. 6. X-ray diffraction profiles of four continuously reduced catalysts derived from the same feedstock. Feed rate and reduction temperatures were held constant. The H₂-stoichiometry was varied. 6a, H₂ = 1.82X; 6b, H₂ = 14.6X; 6c, H₂ = 10.9X; 6d, H₂ = 9.1X.

fraction could be altered by the reduction process.

CONTINUOUS REDUCTION—ACTIVITIES

To test the activity of catalysts made from a common green material the hydrogenation of undistilled tallow fatty acids was chosen. It was believed a more "demanding" application; one that would more easily illuminate differences in the finished catalysts.

A rotating kiln reactor was used to produce a large number of samples, and possible variations in crystallite size or Ni/NiO ratio were produced by small variations in reduction zone temperature but large variations in feedthrough rate and hydrogen stoichiometry. Two feed rates, 225 g/hr and 450 g/hr, were used while the stoichiometric ratio of H₂ could be continuously varied. The iodine value efficiency, already defined, was used to measure the activity of these experimental catalysts. The finished materials were all protected by hard fat, the protected products usually having a nickel analysis of ~10.5-11.5% Ni. The IVE of the experimentally manufactured catalysts are listed in Table IV, with reactor and crystallite size data on selected samples.

Variation in reduction zone temperature appeared to cause only minor variation in crystallite size if the H₂-stoichiometric ratio was low. The difference in D(111) for catalysts made at the high H₂-stoichiometric ratios was more striking and as the analysis indicates the data produced had more consistency. The data are suggestive—it appears that H₂-stoichiometry performs a greater role in producing an active catalyst than does variation in reduction temperature. We investigated this hypothesis using the same green material but reducing at ~470 C with decreasing values of the H₂-stoichiometric ratio. The data for fatty acid hydrogenation using these catalysts is shown in Table V. In Figure 6, a composite of the x-ray diffraction spectra for these experiments is shown.

Neither Ni/NiO-ratio nor D(111) gives a clear quantitation as to how well the nickel is reduced. Given uniformity of movement of feedstock we would expect that the lower the stoichiometric-H₂ ratio the lower would be the efficiency of reduction of NiO. In fact, all the catalysts made at a H₂-stoichiometry of 18.2X had quite high IVEs.

The highest IVE obtained using the commercial catalyst tested was 85.4 ± 0.3%, for G-53. This particular catalyst (see Table I) has a relatively large crystallite dimension (83 Å) but appears quite efficiently reduced having a Ni/NiO ratio of 6.78. The wet-reduced catalyst, PVO, has a quite high Ni/NiO-value but is not very active compared to G-53 or KE/KTR.

All the continuously reduced, experimental catalysts had higher IVE values than the commercial catalysts tested, and all had quite small crystallite dimensions, although the smallest D(111)-value did not produce the highest activity.

What these data do show, however, is that crystallite dimension and the relative efficiency of reduction (Ni/NiO) play a major part in defining activity. It is also apparent that for a given feedstock rate the product from a continuous reducer can be modified in crystallite dimension and Ni/NiO ratio. The nonselective activity for fatty oil hydrogenation will correlate to these parameters.

X-ray diffraction examination of the crystallite radius of catalysts does not afford a sound method of indexing catalysts if they are reduced onto different supports. For a fixed nickel salt/support system, x-ray diffraction measurements can be used to predict relative net activities for fatty oil hydrogenation.

Because x-ray diffraction is a simple analytical tool and is quite fast in execution, its use as a reactor management tool is, clearly, to be recommended.

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