Structural features of evaporated nickel films on oxide supports

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Abstract. Nickel was vacuum-deposited at high temperature (1000–1600°C) on alumina and at room temperature on Hiflosupercel (diatomaceous earth). Light microscopy/Scanning electron microscopy/Energy Dispersive x-ray analysis investigations on the coated materials indicate structural features such as uniform dispersal and firm binding of nickel crystallites on the oxide surfaces and suggests that the feasibility of vacuum technology may offer certain advantages over the conventional processes for making dispersed metal catalysts.

Keywords. LM/SEM/EDAX; vacuum deposition; catalyst structure; nickel; alumina; hiflosupercel.

1. Introduction

Technically important metallic catalysts always contain the metal in a high state of dispersion (Anderson 1975) to maximise the available surface area for a given mass of metal. In many cases, this can be best done by distributing the metal on a support in such a way as to impart to the metallic particles mechanical stability and accessibility to reactant. These attributes in the case of a supported metal catalyst are realised by depositing the metal on to the support so that atoms or atomic aggregates (particles/crystallites) of the metal are physically adsorbed on the support. Oxide surfaces provide a suitable environment for such binding of metal particles under appropriate conditions of deposition. The amount of the metal so adsorbed on a support will depend primarily on the available surface area of the latter. Hence, high porosity oxide supports such as silicas, aluminas and zeolites (alumino-silicates) are conventionally used in making dispersed metal catalysts.

Technical catalysts were prepared through aqueous solutions and subsequently subjected to high temperature treatments for converting the metal radical in the compound to the elemental form. Many processes are described in the literature on catalyst preparation (Anderson 1975). These are based on various theoretical and empirical considerations. However, the great variety of known and unknown, complex, physico-chemical processes involved in the electrolytic and thermal environments during the preparation of the catalysts present problems in the characterisation of the product and realisation of its expected/potential structural integrity and performance.

One of the major problems in this context appears to be the physico-chemical behaviour of hydrated oxide surfaces which can involve a variety of undesirable changes in the expected catalyst integrity before and after high temperature treatment.

The grain growth, porosity, substantivity and crystal orientation of vacuum-deposited films are governed by fairly known and controllable parameters (Holland 1979) such as the nature of the support/evaporant interface, vacuum level, temperature of the support and rate of deposition. Hence, ultrathin evaporated metal films on various supports are used as models for studying the reaction kinetics of highly dispersed catalysts (Anderson 1975). Such films can be prepared with average crystallite diameters from several nanometers down to about 0.5 nanometers (5 Å). The structure of extremely fine particles is inferred from observations made on larger particles produced under appropriate conditions of deposition.

Thicker films depicting higher levels of metal loading are also used in catalytic reactions, in place of inadequately defined technical catalysts.

With a view to ascertaining the feasibility of a new approach to making nickel catalysts, nickel was vacuum-deposited on alumina and Kieselguhr (Hiflosupercel) in the Edward's Coater and LM/SEM (S4-10 Stereoscan)/EDAX (Links 290) investigations made on the coated materials along with a nickel/Kieselguhr catalyst made by chemical precipitation.

2. Materials and methods

2.1 *Coating of alumina*

A tall glass tube was kept inside the work chamber of the Edward's coater and a tungsten spiral heater located inside, very close to the bottom of the tube. Powdered sample of alumina (2 g) was mixed with nickel powder (2 g) and the mixture poured over the heater to submerge it. Since alumina degases profusely under vacuum, the chamber was evacuated gradually for preventing the alumina particles from jumping out of the glass tube. After an hr, a vacuum level of 10^{-4} torr was attained. The temperature of the heater was then suddenly raised (about 1600°C). Further degassing of the alumina at the higher temperature produced adequate turbulence and simultaneous evaporation of the nickel particles facilitated alumina coating. During coating, the vacuum level was about 10^{-3} torr.

2.2 *Coating of Hiflosupercel*

Hiflosupercel (2 g) was taken in a conical glass flask fabricated to fit the Rotatilt accessory of the Edward's coater. A tungsten basket heater containing 100 mg nickel powder was located at the centre of the flask. The work chamber was gradually evacuated to a level of about 10^{-4} torr while holding the flask horizontally in the rotatilt. The flask was rotated so that the Hiflosupercel powder spread out uniformly inside it, due to centrifugation. The heater was switched on and the material was coated with nickel.

The coated and uncoated samples of alumina and Hiflosupercel together with the technical catalyst sample were mounted on a large SEM stub using a double-sided cellotape, coated with silver and examined at 30 kV. Electron micrographs were made at magnifications of $\times 1400$ and $\times 7000$.

EDAX of the samples were carried out at 30 kV. The coated and uncoated Hiflosupercel and the technical catalyst were further examined under the light microscope and light micrographs were made at a magnification of $\times 350$.

3. Results

3.1 Nickel/alumina sample — SEM appearance

Figure 1 shows the surface of an uncoated alumina particle, which presents a bald appearance. Figure 2 shows the surface after the deposition of nickel at high temperature (about 1000 to 1600°C). The nickel deposit depicts the growth of randomly oriented and well separated needle-shaped crystals (0.5 to 2 μm) with some spherical particles which may be from the unevaporated portion of the nickel powder used in the process. The crystallite topography depicts a high degree of porosity which is better depicted at a higher magnification in figure 3.

3.2 Nickel/Hiflosupercel sample — SEM/LM appearance

Figure 4 shows the surface of a platelet of the uncoated Hiflosupercel with its characteristic porosity. A similar platelet coated at normal temperature is shown in figure 5. The nickel deposit cannot be identified on the surface of the platelet since it may consist of crystallites a few Angstroms in size. Figure 6 is a light micrograph of the uncoated Hiflosupercel and shows the platelets to be almost transparent. Figure 7 shows the dark appearance of the coated platelets. It is noteworthy that the nickel coat is very uniform but has not clogged the pores of the platelet.

3.3 Conventionally prepared Nickel/Kieselguhr catalyst sample — SEM appearance

Figure 8 is an electron micrograph of the sample and shows thick slurry-like deposits of nickel on the Kieselguhr platelets, the pores of which are almost completely clogged. Figure 9 (light micrograph) shows a dark platelet with clogged pores, similar to those seen in figure 8. A large number of other platelets seen in figure 9 are almost uncoated and appear mostly transparent. Thus the deposition of nickel in the sample appears to be irregular and nonspecific.

3.4 Nickel/alumina, nickel/Hiflosupercel and technical catalyst — EDAX

Figure 10 shows the EDAX plots of the three samples. In spite of the large nickel crystallites covering the alumina surface (figures 2 and 3) the nickel/alumina sample shows a large AlK_α peak (figure 10). The small NiK_α peak for this sample gives a surface concentration of nickel of only 6%. These two observations indicate that the deposit of nickel on alumina has a high porosity and that the growth of the nickel crystallites may be perhaps in the form of inverted pyramids, with the apexes on the alumina surface.

The EDAX of the nickel/Hiflosupercel sample also shows a large SiK_α and a small NiK_α peaks for the fine grained uniform deposit (figures 5, 7) and gives 7% surface concentration of nickel indicating that the surface of Hiflosupercel is very uniformly covered by the thin grained nickel deposit.

EDAX of the technical sample of figure 8 shows a surface concentration of about 75% indicating that the sludge-like nickel deposit of figures 8 and 9 is much thicker than what can be obtained by adsorption at the Kieselguhr surface.

As regards cleanliness of the products, the EDAX of the vacuum-deposited samples nickel/alumina and nickel/Hiflosupercel show only trace quantities of iron contamination coming from alumina and chlorine coming from Hiflosupercel. On the other hand, the chemically prepared technical sample shows more contaminants such as sulphur, chlorine, calcium and iron.

Figures 1-2. $\times 1400$ SEM appearance of 1. alumina surface 2. nickel crystallites on alumina surface.

Figures 3-4. $\times 7000$ 3. Cf - figure 2 . 4. SEM appearance of a Hiflosupercel platelet.

Figures 5-6.5. SEM appearance of a Hiflosupercel platelet coated. $\times 7000$ 6. LM appearance of Hiflosupercel platelets - platelets look almost transparent. $\times 350$

4. Discussion

Vacuum evaporation is a rapid process and provides uniform coatings of a wide range of metals and compounds on intricate surfaces (Holland 1970). With the exception of antimony, metals are monatomic in the vapour phase and under high vacuum conditions, a metal on a support can condense atom by atom.

Vacuum deposition is a condensation/reevaporation phenomenon and a vapour atom has an average life (residence time) on a surface. Residence time increases with the force of binding between the atom and the supporting material and decreases with temperature. Longer residence time increases the probability of condensation. The binding force between the condensed atom and the support determines the substantivity and structure of a vacuum evaporated film at a given temperature.

Condensation of metal atoms on a support commences by nucleation. On an inert surface an atom migrates randomly prior to reevaporation. If such an atom collides with another to form a pair, the energy required for the reevaporation of

Figures 7-8 : 7. LM appearance of Hiflosupercel platelets showing the uniform, opaque deposit of nickel metal which has not clogged the pores. $\times 350$. 8. SEM appearance of a conventionally prepared (technical) nickel/Kieselguhr catalyst – copious, slurry-like deposits of nickel completely clogging the pores of Kieselguhr platelets. $\times 7000$.

Figure 9. LM appearance of catalyst of figure 8 showing thick nickel deposit on one platelet whereas the other platelets are very little coated.

the pair being higher, the atoms may condense. Reevaporation is favoured at higher temperatures and so nucleation commences with larger aggregates of metal atoms. Thus, metallic films formed on inert or contaminated surfaces are made up of larger crystalline aggregates and have low substantivity to such surfaces.

Nucleation on active surfaces is rapid and less temperature dependent. In an active surface an atom is quickly condensed by adsorption. Aggregation can also take place by collision of another atom with such a bound atom. However, since an active surface may provide a large number of sites for adsorption, the vacuum evaporated film of a metal on such a surface has a finer structure and a greater substantivity than that deposited on an inert one and aggregation may commence only at very high temperatures.

Any solid can be used as a catalyst support for dispersed metal. However, oxide surfaces such as those of alumina and silica, being active, are better suited for the adsorption of a metal such as nickel. The surface activity however, causes larger amounts of water adsorption/retention when these materials are exposed to humid atmosphere or impregnated with aqueous solutions and the active sites get neutralised. Such retention is particularly severe with alumina and hydrated alumina requires heating to 1000°C over prolonged periods for complete activation (Kirchner 1978). Silica can be activated by heating to about 500°C. For highly porous aluminas and silicas complete dehydration is very difficult and may require higher temperatures, which would in turn alter the porosity of the materials.

Use of vacuum or glow discharge (Holland 1970) for desorption of water from such materials helps in obtaining substantial degrees of surface activities at lower temperatures of activation and has particular significance for vacuum evaporated film catalysts. In the present study use of glow discharge was avoided for maintaining the activity of the alumina/silica surfaces in their native state and dehydration was carried out under vacuum (10^{-4} torr) at normal temperature.

Further degassing of the alumina during the coating process at about 1000–1600°C produced a sufficiently large amount of active sites to give a porous but dense deposit of nickel (figure 2). Figure 3 more clearly depicts how well separated and firmly

Figure 10. EDAX plots of Ni/alumina and Ni/Hiflosupercel samples made by vacuum evaporation and Ni/Kieselguhr sample made by chemical precipitation. $\times 350$

bound the large (0.5 to 2 μm) crystallites are. These crystallites appear to have grown upwards from the alumina surface by coalescence of the atoms of nickel with condensed nuclei on the alumina surface. Thus, the surface coverage of alumina by nickel should be much less than what is indicated by figures 2 and 3. This fact is well borne out by the EDAX of the coated sample (figure 10) which, despite the apparent dense and thick coat of the crystallites of figures 2 and 3, shows a very large AlK_α peak and a tiny NiK_α peak. Thus the surface concentration of nickel of only 6% as obtained from the plot is indicative of the large alumina surface which is still available for further loading of nickel. The objective behind the use of high temperature and high nickel proportion (50%) in the nickel/alumina powder charge was to form large crystallites for SEM investigations on growth and structure of the deposit formed. This purpose has been served as described above.

The coating of Hiflosupercel is representative of the vacuum deposition of nickel on an oxide surface at normal temperature and a high degree of dehydration (as compared with alumina). The deposit consists of particles which are at least smaller than about 300 $\text{\AA}$ (30 nm) (figure 5) and is extremely uniform and adequately dense (figure 7). The clear pores of the Hiflosupercel platelets in figure 7 also indicate that in all probability the binding of nickel to silica is specific (adsorption) and firm as with alumina (figures 2 and 3). In spite of the large silica/nickel ratio used in this process (2 g silica/100 mg Ni) EDAX gave 7% surface concentration of nickel which is slightly higher than that in the case of nickel/alumina. This is perhaps indicative of the large surface coverage of the Hiflosupercel by a fine deposit of nickel crystallites.

Metal films evaporated on to substrates could show the presence of oxides to some extent (Holland 1970). This oxidation is believed to be caused by the collision of metal atoms with residual oxygen or water vapour in the coating chamber. However, since a catalyst prepared by vacuum evaporation has primarily a finely-dispersed metallic structure, reduction of the material is likely to be a much simpler and less severe operation than is involved in reducing the supported metal oxides of a conventional catalyst and may thus help in reducing sintering which is involved in the latter case.

Vacuum-deposited nickel has been found to be non-pyrophoric and hence, can also facilitate batch production and storage like the conventional catalyst (oxide), prior to reduction/activation.

In catalysts prepared by impregnation, two processes occur, namely adsorption of the metal ion to the carrier surface and occlusion (mechanically held) of salts in the carrier pores (Anderson 1975). Ion adsorption methods give a more uniform distribution of metal on the available surface of the support. Under appropriate conditions, such specific binding facilitates about 5–10% loading of nickel on high area materials such as alumina and silica. Occluded material increases the degree of sintering during subsequent high temperature treatments (calcining, reduction etc.) and can deactivate the dispersed metal catalyst by direct pore blockage and formation of reaction products.

Thus metal loading of active supports beyond the adsorption levels may be detrimental to the structural stability, performance and life of a catalyst product and may signify superfluous material costs.

Figure 8 shows the SEM topography of a nickel/Kieselguhr catalyst and depicts completely clogged platelets of Kieselguhr and massive deposits of nickel oxide. The in-process and in-use stability of such a structure appears doubtful.

Figure 9 shows the LM appearance of the sample. It may be noted that only one support platelet shows a thick deposit almost completely blocking the pores. Most of the Kieselguhr platelets in figure 9 have received very little deposit.

The magnitude of the nickel deposit (figure 8) suggests a non-adsorptive or mechanical binding of nickel to Kieselguhr. EDAX of the sample gives 75% surface concentration of nickel. Hence the chemical precipitation of a high amount of nickel on Kieselguhr appears to have generated a combined supported and partly unsupported catalyst structure whose stability is doubtful under the subsequent thermal treatments.

Development of a technological process for the commercial production of vacuum evaporated nickel/metal supported catalysts is perhaps a future event. The chemistry of an oxide surface in contact with water is quite complex (Anderson 1975). Hence ion adsorption at a hydrated oxide surface may involve a variety of possible processes. Solubilities of the solid oxides during impregnation/precipitation cannot often be ignored. Besides, the conditions of calcination/reduction in making supported nickel salts might affect the structural integrity of dispersed catalysts.

These hydrothermal conditions could be optimised in making nickel catalyst by vacuum evaporation.

5. Conclusions

SEM examination of nickel, vacuum evaporated on alumina surface at high temperature (1000–1600°C) shows the formation of a uniform, porous deposit of distinct crystallites. LM examination of nickel vacuum evaporated on Hiflosupercel (diatomaceous earth) at room temperature indicates the formation of a uniform and firm coating of nickel on the plates of Hiflosupercel. EDAX of the coated materials also suggest the formation of porous films on the two oxide surfaces. In contrast, similar LM/SEM/EDAX investigations on a conventionally-prepared nickel catalyst indicate the formation of a slurry-like deposit of nickel, which is rather weakly bound to the Kieselguhr support and appears to clog the pores of the latter. The superior structural features of these vacuum-evaporated films and the possibility of making them in a controlled manner, suggests that vacuum technology may offer advantages over conventional technology for making dispersed metal catalysts.

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References

- Anderson J R 1975 *Structure of metallic catalysts* (London, New York: Academic Press) Chapters 1, 2, 4
- Holland L 1970 *Vacuum deposition of thin films* (London: Chapman and Hall) Chapter 7
- Kirchner J G 1978 *Thin layer chromatography* 2nd edn., (New York: John Wiley) p. 36