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Electroless plating : a technique for the preparation of supported cobalt and gold catalysts

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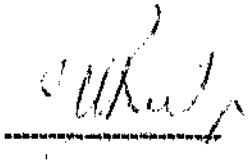
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DECLARATION

I declare that the work presented in this dissertation was carried out exclusively by myself under the supervision of Professor N.J. Coville. It is being submitted for the degree of Master of Science at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other university.



Johannes Albertus Beetge

Cobalt catalysts prepared by electroless plating showed activity towards the partial oxidation of methane to carbon monoxide and water, with conversions of about 60% under the conditions employed.

ABSTRACT

The preparation of supported cobalt and gold catalysts by the technique of electroless plating, and the establishment of the influence of synthesis variables on the physical properties of the supported catalyst, forms the basis of this dissertation. In both the cases of cobalt and gold supported on extruded cylindrical alumina pellets, the penetration profile of the metal into the support showed dependence on the pH of the activation solution, while the metal loading onto the same support showed no dependence on pH of the activation solution at all.

The variables involved in the plating process of the activated pellets, namely: i) the concentration of the activation solution, ii) pH and temperature of the plating bath, iii) plating time, and iv) variation of the concentrations of components of the plating bath all influenced the mass of metal loaded onto the support, but not the penetration characteristics. It is therefore possible to prepare a supported catalyst with very specific properties using the above information.

Under similar conditions, with extruded alumina pellets as support and with the specific plating formulations used, gold showed higher metal loadings at lower gold concentrations than cobalt.

ELECTROLESS PLATING: A TECHNIQUE FOR THE PREPARATION OF SUPPORTED COBALT AND GOLD CATALYSTS

Johannes Albertus Beetge

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ELECTROLESS PLATING: A TECHNIQUE FOR THE PREPARATION OF SUPPORTED COBALT AND GOLD CATALYSTS

Johannes Albertus Beetge

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1.4 Cobalt in catalysis.

1.4.1 Introduction

Cobalt is a metallic element, and, with iron and nickel, it is one of the first-row transition-metal members of group 9 of the periodic table. Cobalt has an atomic number of 27, and a relative atomic mass of 58,9332. It has only one stable isotope that occurs naturally, with 12 radio-active isotopes with mass numbers between 54 and 64 (1).

Cobalt is the thirtieth most abundant element on earth and comprises approximately 0,0025% of the earth's crust (2).

Very little cobalt metal was used until the 20th century, but evidence exists that its ores have been used as long ago as 2600 B.C. as colouring agents for glass and pottery (1,2). In the sixteenth century, this property of cobalt was rediscovered. Metallic cobalt, isolated in 1735 by G. Brandt, a Swedish scientist, was in 1780 shown by T. O. Bergman to be an element. The use of cobalt as a metal dates from 1907, when a series of cobalt-chromium alloys were patented. These were the fore-runners of modern superalloys. It was shown in 1930 that cobalt added to certain alloys of iron, nickel and aluminium enhance their properties as permanent magnets (1,2).

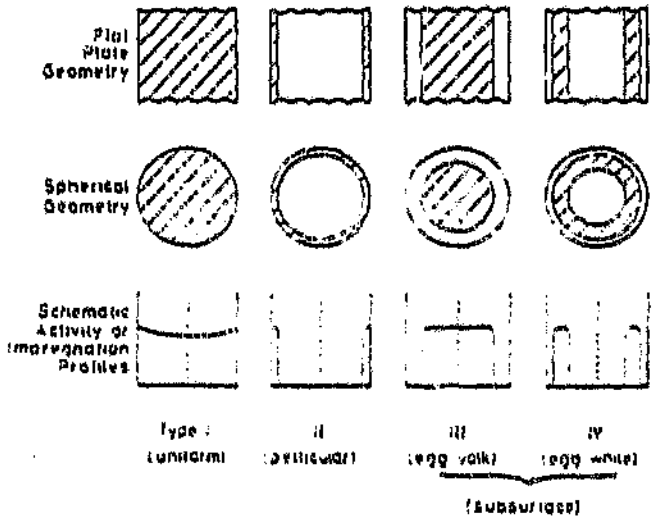


Figure 1.1 Four limiting types of impregnation or activity profiles. Hatched areas in the cross sections of slabs and pellets (top and middle rows) indicate the regions where active components are deposited. The bottom row shows schematic examples of impregnation or activity profiles (28).

hypophosphite, formaldehyde, hydrazine, borohydride, amine boranes and certain derivates of these.

2) A buffering reagent to maintain the bath pH. Buffering is important since the plating rate and the stability of the bath may be very sensitive to pH.

3) A complexing agent for the metal ion. Many electroless baths operate under alkaline conditions, making the presence of a complexing agent for the metal ion essential.

4) Stabilizers, to prevent spontaneous decomposition of the bath. Many electroless plating baths are thermodynamically unstable.

5) "Exaltants", which may be used to accelerate the deposition rate of the metal.

1.3 Metal support impregnation.

The metal loading profile of a supported catalyst is an important factor in determining kinetic parameters and product distributions (23,24). Impregnation and drying steps involve mass and/or heat transfer processes which often do not reach equilibrium, resulting in non-uniform concentration profiles of impregnation along the radius of the support pellet (25). Examples of these impregnation profiles, along with activity profiles, are shown in figure 1.1.

The Type I profile is sometimes referred to as "uniform", although the metal concentration may not be constant with respect to pellet radius, as shown schematically in figure 1.1. Type II is often referred to as "pellicular" or "egg-shell", Type III as "egg-yolk", and type IV as "egg-white". Types III and IV, in which bands devoid of catalytic material occur on the exterior of the support pellet, are also termed "subsurface impregnation" types (26,27). It is of considerable industrial as well as academic interest to predict and control these impregnation profiles.

The reducir , action occurs only on a catalytic surface. Once deposition is initiated on a surface, the metal being deposited must itself be catalytic in order for deposition to continue. Electroless plating will occur directly on some metals (e.g. gold and the platinum group metals) and on other metallic and non-metallic surfaces which have previously been made catalytic by a suitable activation treatment (7).

Useful electroless deposits have been produced of nickel, cobalt, palladium, platinum, copper, gold, silver and as a variety of alloys involving one or more of these metals (8).

Since electroplating is generally cheaper than electroless plating, any advantages of the latter normally relate to specific properties of the metal film itself. Electroless deposition is usually applied because it provides one or more of the following advantages over electrodeposition:

1) More uniform deposits are produced.
2) Deposits are often less porous.
3) No external electrical current is needed.
4) Deposits can be produced directly upon non-conductors.
5) Deposits have unique chemical, mechanical or magnetic properties (9).

Electroless plating baths are invariably aqueous solutions. The bath components include some or all of the following:

1) A reducing agent, which is the source of electrons for converting metal ions to metal atoms. Chemical reducing agents successfully utilized for electroless plating include

1.2.5 Other methods of catalyst preparation

Most of the catalysts prepared in industry and in the laboratory are prepared by the three methods described above. Some catalysts with special applications are prepared by other methods. These methods include:

1) decomposition of metal clusters,
2) chemical deposition from metal colloids,
3) ion implantation,
4) metal vapour deposition,
5) thermal fusion,
6) chemical reaction and
7) electroless plating.

Since the method of electroless plating has been used extensively in this thesis, the procedure is discussed in more detail below.

1.2.6 Electroless plating.

The process of electroless plating was first reported in 1946 by Brenner and Riddell (6). It involves the autocatalytic reduction of dissolved metal ions to produce a coherent film of metal. This process provides a continuous build-up of metal coating on a substrate by simple immersion in a suitable aqueous solution, without the passage of an external electrical current. For converting metal ions to the elemental form, a chemical reducing agent has to be present in solution.

1.2.3 Impregnation

This is one of the most widely used preparation methods. In impregnation by immersion, the support is usually dried, evacuated to remove air in the pores, and brought into contact with an excess of an impregnating solution containing metal salts. The solid is then dried and calcined. Because of strong adsorption of ions on high surface-area supports, the adsorption equilibrium between support and solutions at various concentrations must be determined before impregnation to obtain the desired concentration of metal on the support. Impregnated catalysts have several advantages over precipitated catalysts. They are more economical because they require smaller amounts of the usually expensive active components than do precipitated catalysts. Because supports are commercially available in almost every desired range of physical and chemical property, the impregnation methods permit production of supported catalysts appropriate for the reaction conditions prevailing in a given reactor.

1.2.4 Ion exchange

This involves the exchange of support ions with ions, often of higher valency, in solution. Ion exchange can also be used to remove catalytic poisons or to add promoters. For example, ammonium ions in solution will replace impurities such as sodium ions in a catalyst. Catalysts can also be loaded or modified by ion exchange mechanisms.

properties that determine its activity. The whole history of catalysis reveals that preparation plays an important role in catalyst behaviour. Quite often, the specific methods used in the preparation of catalysts are only found in the patent literature, or are regarded as trade secrets. This has hindered the development of catalysis as a quantitative science. There is a need for strict quality control of the raw materials used in the preparation of a catalyst because even trace impurities in the catalyst can often modify catalytic performance.

The most important methods used for the preparation of supported catalysts are discussed on the following pages.

1.2.2 Co-precipitation

This method involves the following steps:

1) preparation of chemical solutions with desired components,
2) complete mixing of the solutions, and formation of a precipitate,
3) removal of the precipitate by a suitable method, like filtration or centrifugation, and
4) washing, drying, calcination and pretreatment to activate the catalyst.

A solid solution of variable components is obtained, in which the metal is uniformly distributed on the surface as well as in the bulk.

surface area. The preparation of supports with controlled surface area, pore volume and pore size distribution has been the subject of much research over the past years. In the preparation of a supported metal catalyst, it is important to maximize metal dispersion and to maintain such dispersion during reaction in order to assure maximum catalytic activity and activity maintenance (5). Some methods commonly used for the preparation of supported catalysts are discussed below.

1.2 Catalyst preparation

1.2.1 Introduction

From a chemical perspective catalytic processes differ from ordinary chemical reactions because of the participation of an additional reactant, the catalyst, which does not appear in the stoichiometric equation. However, the nature of a catalyst often determines the products of a chemical reaction.

In many catalysts, the active material is the minor component. The active ingredient is generally supported on a more or less inert carrier. This support serves to disperse the active component over a large surface area, and to supply mechanical form and strength to the catalyst.

Despite the widespread use of catalysts in industry, the preparation of catalysts is more often an "art" than a "science". Catalysts with the same chemical and physical properties may often differ in behaviour, indicating that these properties are not necessarily the only

A catalyst can only accelerate a thermodynamically feasible reaction, but cannot alter the position of the thermodynamic equilibrium of reversible reactions. A given catalyst will not necessarily catalyse equally all or several of the possible reactions in a reaction mixture. By selective choice of catalyst, only the desired reaction need be accelerated. This ability of a catalyst to enhance only a specific reaction, has led to the widespread use of catalysts in the chemical industry.

In heterogeneous catalysis, the catalyst is usually in the solid phase, while the reactants are gases or liquids. Separation of reaction products from the catalyst is easy, but only surface species of the catalyst can participate in the reaction. Reproducibility in heterogeneous catalysis is poor, because of variations in the structure of catalytic sites. Selectivity is also poor, because several types of active sites can be present, for example in the form of surface defects.

Homogeneous catalysts are usually well-defined chemical compounds or co-ordination complexes that can be dispersed molecularly in a reaction medium together with one or more of the reactants. Separation of products from reactants can be costly and difficult. However, good reproducibility due to definite structure and stoichiometry of catalytic centres is possible.

Supported metal catalysts are one of the most common forms of heterogeneous catalysts in use today. They consist of a catalytically active metal dispersed on a porous support of high

work laid the foundation for chemical kinetics as we know it today (1).

At the turn of the century, Ostwald recognized the true significance of the functioning of a catalyst. He defined a catalyst as a substance which alters the velocity of a chemical reaction without appearing in the end products. Ostwald's concept served to put catalysis on a measurable basis for the first time, and marked the beginning of the science and technology of modern catalysis.

In the following years, just as the principles of chemical equilibrium and kinetics were becoming known, the field of catalysis became more quantitative and developed rapidly. In 1909, F. Haber demonstrated the synthesis of ammonia from its elements on an osmium catalyst at high pressure. Haber and co-workers worked out methods of catalyst testing and process development that are essentially the methods of choice today (4). In about 1920, Franz Fischer and Hans Tropsch converted mixtures of carbon monoxide and hydrogen to oxygenated compounds on alkalized iron catalysts, and on improved Fe, Co and Ni catalysts to hydrocarbons suitable for motor fuels (1). Between 1936 and 1945, Ruhrchemie AG licensed 12 Fischer-Tropsch (FT) plants with a total capacity of about 1 million tons per year of FT products, mainly gasoline and diesel fuel. In 1954, the FT process was licensed to the South African Coal, Oil and Gas corporation Limited (SASOL). FT plants in France, in the United States and in Germany after World War II had to capitulate in the mid-fifties in the face of cheap mineral oil and its ready processing. Consequently, SASOL has been the predominant producer of FT products for over 25 years (1).

of cobalt and gold, the metals that have been studied in this thesis. The survey is not meant to be comprehensive but is included to put the thesis work in perspective. The two catalytic reactions used to test the new electrolessly plated catalysts are described. These are the hydrochlorination of acetylene to give vinyl chloride in the case of gold, and the partial oxidation of methane to give synthesis gas in the case of cobalt.

1.1 Catalysis - A Review

The term "catalysis" was first used in ca. 1835 by Berzelius, who was one of the great organizers of chemical knowledge of his time (1). He was the first to note that the phenomenon of reaction enhancement observed by his co-workers, was generally related, and that chemical reactivity could be induced by outside agents, without the agents apparently taking any part in the reactions. He called this general phenomenon "catalysis".

The earliest applications of catalysts were in the production of wine, vinegar and soap, which have been produced since ancient times. The first industrial application of catalysis mentioned in the literature was the preparation of ether by distillation of "spirits" in the presence of sulphuric acid (2).

In 1831, P. Philips reported the use of platinum as catalyst for the oxidation of sulphur dioxide. C.F. Kuhlman reported in 1838 the oxidation of ammonia to nitric acid in the presence of platinum (3). During the next 60 years, the work of Wilhelmy and Berthelot stands out. They studied the hydrolysis of cane sugar and of esters respectively. Their later

CHAPTER 1

INTRODUCTION

This thesis describes the use of a novel method of catalyst synthesis, namely electroless plating. This procedure is commonly used in the micro-electronics industry, but has been little explored in catalyst synthesis.

Indeed preliminary studies on the synthesis of electrolessly plated cobalt catalysts on alumina were investigated in the laboratories of the University of the Witwatersrand during 1991 by a graduate student, Dr. Saul Colley. At the time, a preliminary review of the literature revealed that there was little awareness of this technique by catalyst scientists. Since then, some earlier work on this technique has been cited, and some recent reports by other catalytic groups have appeared in the open literature.

This thesis continues on from the work of Dr. Colley. Prior to the discussion of the experimental work performed in this thesis, this chapter will highlight some of the important issues which provide background to the experimental data collected and analysed.

Thus, this thesis contains a brief discussion of the general methods used in the synthesis of supported catalysts. This is then followed by a discussion of some of the catalytic properties

CHAPTER 2

EXPERIMENTAL

2.1 Bath preparation: electroless cobalt plating.

Several formulations for preparing cobalt plating baths were described by Pearlstein (9). The formulations mentioned were mostly evaluated for physical characteristics, like magnetic properties, coercive force, film thickness, preferred direction of magnetism and deposition rate. The use of electroless plating as a method for the preparation of supported metal catalysts was never mentioned in his formulations.

Pearlstein was not concerned about the chemical analysis of the metal deposits obtained. According to him, the production of electroless cobalt plating baths were found to be more effectively controlled by observation of the magnetic properties of deposits than by chemical tests.

Electroless cobalt plating baths evaluated by Pearlstein are shown in Table 2.1.

In this thesis the following issues have thus been explored:

1) Electroless plating baths are almost without exception aqueous solutions, containing some or all of the following: a metal salt, a reducing agent, a complexing agent for the metal ion, stabilizers, exaltants and buffering agents. The influence of varying the concentrations of the above as they relate to penetration and metal loadings of cobalt and gold has been investigated.

2) Conditions under which a plating bath is operated, can determine the extent of plating obtained. The effects of variation in temperature and pH of the plating bath on metal loadings and penetration profiles have been investigated.

3) The use of supported cobalt catalysts, prepared by the process of electroless plating, in the partial oxidation of methane has been investigated.

4) The use of gold catalysts, prepared by electroless plating, in the hydrochlorination of acetylene, has been investigated.

volatile compounds. This was not experienced with gold as a catalyst (22).

1.6 Aims of this thesis.

Electroless plating as a method for the preparation of supported catalysts has to date not received much coverage in the literature. The process is used extensively in industry where exact plating bath formulations have often been concealed as they have been regarded as trade secrets. It has further been reported that plating baths are unstable, very sensitive to impurities at concentrations of 1 ppm or less, that the behaviour of plating baths can be unpredictable, and that published formulations may not work in everyone's hands (7).

Preliminary work in the Chemistry Department at the University of the Witwatersrand has revealed that electroless plating can enable the preparation of supported catalysts with unique properties, while maintaining control over the exact metal content and the penetration profile of the support (28). In this early work, it has been shown that electroless plating can occur directly on the surface of catalytic metals. (For non-catalytic metals, a pre-treatment with a catalytic material is needed to give a surface on which autocatalytic reduction can commence.) Although not described in the literature, the preliminary studies carried out in our group have shown that specific bath solution properties used in the pretreatment process, have a profound effect on the penetration profile of the metal on the support. Indeed the preliminary data suggested that the penetration profile, and therefore the thickness of the metal layer, can be carefully controlled.

Vinyl chloride was first prepared from the reaction of dichloroethane with alcoholic potash. On prolonged exposure to sunlight in a sealed tube, white flakes from the vinyl chloride started to form. This white solid was first studied in 1872 and was described as having an empirical formula $(C_2H_3Cl)_n$ (21).

A patent was obtained in 1912 for the use of mercuric chloride as a catalyst for the reaction between hydrogen chloride and acetylene, and an effective industrial route to vinyl chloride was established. Vinyl chloride monomer was first produced commercially in the 1930's via this route, with acetylene derived from calcium carbide. As demand for vinyl chloride increased, more economical feedstocks were sought. After ethylene became plentiful in the 1950s, commercial processes were developed to produce vinyl chloride from ethylene and chlorine (21).

Currently, about 6% of world production of vinyl chloride monomer takes place by hydrochlorination of acetylene. The industrial catalyst for this process is currently based on mercuric chloride supported on activated carbon (22). A range of metals were studied as catalysts for the acetylene hydrochlorination reaction. This study dictated that catalytic activity correlated with the standard electrode potential for the metal, and on that basis it was predicted that chlorides of metals with a standard electrode potential greater than that of mercury(II) or palladium(II) would be more active hydrochlorination catalysts. As predicted, Nkosi and co-workers found that on a mole basis gold was about one order of magnitude more active than mercury. The authors also showed that the mercury catalyst reactivated in situ with hydrogen chloride at 180 °C, showed a 25% loss of mercury as

Bimetallic catalysts can show variations in catalyst morphology, and to arrive at meaningful interpretations in trends of activity, it is important to identify which kind of particles make the largest contribution to the metal surface area, and thus carry the main burden of catalytic action. With bimetallic catalysts, consisting of gold added to an active group 8-10 metal, interesting results were obtained. Addition of gold to palladium in a gold-palladium bimetallic catalyst for the hydrogenation of unsaturated compounds, resulted in a decrease in catalytic activity relative to that of palladium itself. In some cases, this loss in activity was partially counterbalanced by improvements in selectivity.

A significant enhancement of the rate of water formation from interaction between hydrogen and oxygen was reported for silica-supported gold-palladium catalysts, with a maximum at intermediate gold content (20).

1.5.3 Hydrochlorination of acetylene.

Vinyl chloride, CH_2=CHCl, by virtue of the wide range of applications for its polymers, is one of the largest commodity chemicals in the United States and is an important item of international commerce. Growth in production of vinyl chloride is directly related to demand for its polymers and, on an energy-equivalent basis, rigid polyvinyl chloride (PVC) is one of the most energy-efficient construction materials available (21). It was not until after World War II that vinyl chloride production grew rapidly as a result of the increased volume of PVC products for the consumer market.

temperatures, provided a good ligand is present to lower the redox potential to below that of water. Gold is thus not attacked by most acids under ordinary conditions and is stable in basic media. Gold does, however, dissolve readily in 3:1 hydrochloric-nitric acid (aqua regia) to form $HAuCl_4$, and in alkaline cyanide solutions in the presence of air or hydrogen peroxide to form $[Au(CN)_2]^-$. These reactions are important for the extraction and refining of the metal. Gold readily amalgamates with mercury (19).

1.5.2 Gold as a catalyst.

Activities of gold-containing catalysts are generally far lower than those of the Group 8-10 metals, or of the other transition metals in Group 1. This lack of activity has been ascribed to the lack of d-band vacancies in gold, but it is by no means clear that this restriction necessarily applies to surface atoms, since high activities for CO oxidation over highly dispersed gold catalysts has been reported. Gold-containing catalysts frequently display improved selectivities (19).

Some work has been done on bimetallic catalysts aimed at correlating the catalytic behaviour and the electronic structure of the catalyst with alloy composition. Alloys of palladium, a group 10 metal, having in excited states a partially unoccupied d-band, and gold with a completely filled d-band were studied and attempts were made to interpret the results on the basis of the rigid band theory. It turned out that the observed catalytic activities could not unambiguously be correlated with increasing occupancy of d-bands in the alloys as function of gold content (20).

activity, and has not been observed to form coke (15). According to Schmidt's observations (18) cobalt deactivates due to phase changes and volatilisation.

1.5 Gold in catalysis.

1.5.1 Introduction

Gold is presumably the first metal known and used by humans. It occurs in nature as a pure metal, and is treasured because of its colour, ductility and corrosion resistance. In the middle ages, the demand for gold led to the intense and unsuccessful attempts of alchemists to convert base metals to gold. It has been suggested that these pursuits provided the basis for the chemical science as we know them today.

Gold has an atomic number of 79, and occurs naturally as a single isotope of mass 197. At least 26 unstable isotopes have been made, the most frequently used is gold 198, with a half-life of 2,7 days. Common oxidation states of gold are 0, 1 and 3 (19).

Gold is widely distributed and the average content in the earth's crust is estimated to be 3.5 ppb. The gold content of ocean water varies considerably with location; investigations indicate that the average value is of the order of 10 parts per trillion, which is well below the concentration (3 ppm) required for economic recovery (19).

Gold is indeed a noble metal. Other than in the atomic state, it does not react with oxygen, sulphur or selenium at any temperature. Gold reacts with the halogens, particularly in the presence of moisture. Gold also reacts with various oxidising agents at ambient

suitable.

For the production of synthesis gas the partial oxidation reaction is thermodynamically more favourable than the steam reforming route. The steam reforming reaction is highly endothermic and is only favourable at high temperatures. The partial oxidation reaction is mildly exothermic and favourable even at low temperatures.

The use of catalysts for the partial oxidation reaction of methane has been reported. Supported nickel catalysts have been studied in detail, and it was claimed by Choudary and co-workers (14) that the use of mixtures of lanthanides and nickel gave conversions of 87,2% and a selectivity to CO of 98%. Mixed oxide catalysts containing chromium, iron, cobalt and nickel were prepared by Hayakawa (15), and both nickel and cobalt were reported to show high activity and selectivity to synthesis gas.

Green and co-workers (16) showed that Ni, Ru, Rh, Pd, Pt and Ir catalysed the partial oxidation of methane. Several other references can be found in the literature of catalytic properties being exhibited by a variety of metals in the methane partial oxidation reaction. The best among them describe the use of noble metals, in particular rhodium and iridium, but it is doubtful if the current world-wide production of these metals can be sustained on a cost-effective basis to provide for their use in large quantities.

The use of nickel for the catalysed partial oxidation reaction results in high activities, but the catalyst shows slow deactivation and results in coke formation (17). Cobalt shows high

Methane is used in a number of industrial applications. It can be used to produce halocarbons in the presence of HCl or HF, or hydrocyanic acid in the presence of ammonia. It is, however, more likely to be used in the direct conversion to synthesis gas (12).

Synthesis gas, or syngas, consists of mixtures of hydrogen, carbon monoxide and carbon dioxide in various proportions. The industrial importance of syngas is twofold: it is a cheap source of hydrogen for processes such as ammonia synthesis, and it can be used as a feedstock for the synthesis of many organic chemicals (13).

Partial oxidation is an option for generating syngas from natural gas. The production of syngas (equation 1.1) can be achieved by steam reforming of methane:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad (\Delta H^\circ_{298} = 206 \text{ kJ/mol}) \qquad 1.1$$

This process produces a hydrogen to carbon monoxide ratio of three as opposed to two obtained for the partial oxidation process shown in equation 1.2:

$$CH_4 + \tfrac{1}{2}O_2 \leftrightarrow CO + 2H_2 \qquad (\Delta H^\circ_{298} = -36 \text{ kJ/mol}) \qquad 1.2$$

Production of synthesis gas via the steam reforming process (equation 1.1) is important in the manufacture of ammonia, which is a large user of synthesis gas worldwide. The higher hydrogen content, however, does not favour other chemical processes, for which the carbon monoxide to hydrogen ratio produced in the partial oxidation reaction may be more

A brief description of the use of cobalt in a specific catalytic reaction, methane partial oxidation, is given below. This reaction was used as a test reaction to test catalysts synthesised in this project.

1.4.3 Partial oxidation of methane.

As the world population increases, the demand for energy will follow. Through the ages, and with increasing technology, the source of energy of man has changed. Wood was replaced by coal during the industrial revolution, and in the latter half of the twentieth century the consumption of oil overtook that of coal. Natural gas, as a source of energy, has never to date been well utilised as a source of energy. Technology and economy have limited its use, mainly because of the problems experienced with its transportation and storage. Even in modern times, the natural gas produced as the by-product of petroleum oil, is often flared (2). The purification of natural gas to methane is relatively simple.

Natural gas is still a usable source of energy, and can be located in most areas of the world. The price advantage of natural gas is diminished by the cost of transportation. It can be transported as the liquid, after being cooled to -162 °C at 8MPa, but cooling consumes energy and will add to the price of transport. Natural gas is often cheaper than alternative carbonaceous raw materials, and therefore attractive for producing synthetic petroleum products (11).

(3) homogeneous catalysts used in the high pressure oxo process for the production of aldehydes and alcohols (2).

The following types of reactions have been catalysed at some stage by cobalt-containing materials: hydrogenation, dehydrogenation, hydrogenolysis including hydrodenitrification and hydrodesulfurization, ammonoxidation, oxidation, hydroformylation, polymerization, selective decomposition and ammonia synthesis. (1)

Cobalt is particularly successful as a catalyst, and it stems from one or more of the following properties:

(1) The facile redox properties of the element, the ability to form stable species in multiple oxidation states, and the ease of electron transfer between the oxidation states via unstable intermediates or free radicals.

(2) The ability to form complexes with suitable donor groups and the relative stability of these complexes.

(3) The ability to form complexes of varying co-ordination number and to exist in equilibrium in more than one stereochemical form.

(4) The ability to undergo equilibrium decomposition reactions in polymerization systems. Decomposition products may take part in the catalysis.

(5) Cobalt complexes are able to undergo ligand exchange reactions which can be important in assisting catalysis.

(6) Cobalt oxides and sulphates, because of lattice vacancies, bond energies or electron effects, are active heterogeneous catalysts. (2)

The worlds largest cobalt reserves are in Zaire, Zambia, Morocco, Canada and Australia. Together the ores of these countries contain over one-half of the world cobalt supply, the richest deposits being found in Zaire and Zambia. Supply is dependent on the political stability of these countries, and therefore cobalt is regarded as a strategic metal and is stockpiled in some countries.

Chemically, cobalt resembles iron and nickel. It shares many common properties with iron and nickel, e.g. a valence of +2 or +3 in most of its compounds. Cobalt has a valence of +1 only in a few nitrosyl and carbonyl complexes.

Cobalt and its compounds have expanded from use as colouring agents in glass and pottery to drying agents in paints, to their use in animal and human nutrients, electroplating materials, high-temperature alloys, radiology, thermistors and explosives. Cobalt is also a very effective catalyst or catalyst component in many homogeneous and heterogeneous processes.

1.4.2 Cobalt as a catalyst.

Over 40% of the cobalt employed in nonmetallic applications is used in catalysis. About 80% of the use in catalytic areas takes place in three areas:

(1) heterogeneous catalysts used in hydrotreating/desulphurization in the oil and gas industry,

(2) homogeneous catalysts used in the production of terephthalic acid or dimethylterphthalate, and

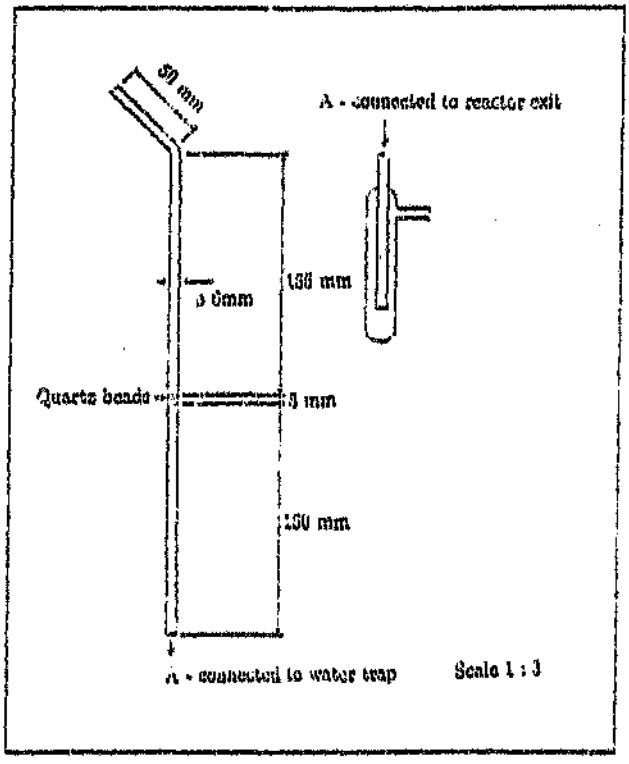


Figure 2.3 The reactor system used, which allowed temperature measurement above the catalyst bed (14).

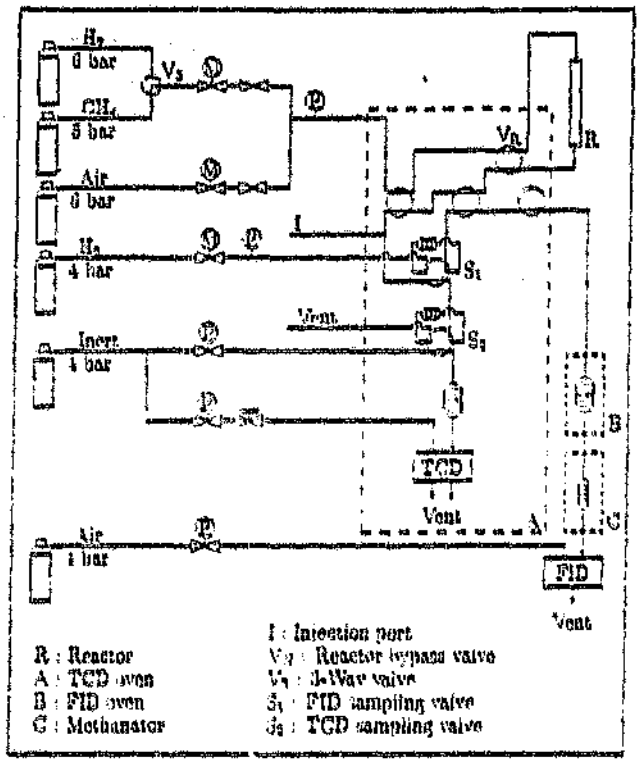


Figure 2.2 The installation used for conducting the reactor studies for the partial oxidation of methane (14).

2.4.2 Atomic absorption spectroscopy.

The concentrations of the relevant metals were determined by atomic absorption spectroscopy (AAS). Samples were prepared for analysis by crushing and grinding the pellets to a fine consistency in a mortar and pestle. A pre-determined mass of sample (± 0,2 g) was accurately weighed on an analytical balance, soaked for 30 minutes in 10 ml. of aqua regia, and then heated for 2 minutes at the boiling point of the liquid.

These were then diluted to an appropriate volume with distilled water, and again diluted to contain a final concentration of cobalt of not more than 10 mg Co/l in the final dilution. A set of standard solutions were prepared from a standard 1000mg Co/l AR-grade solution, to contain concentrations of 2, 4, 6, 8 and 10 mg /l of cobalt respectively. The absorbances off all of these solutions were determined by AAS.

2.5 Catalytic reactor studies.

2.5.1 Partial oxidation of methane.

2.5.1.1 Installation.

The installation used for conducting the reactor studies is shown in figure 2.2.

The reactor used allowed temperature measurement above the catalyst be ., and is shown in figure 2.3. A mixture of methane and air was fed via a system of valves housed in the TCD oven, A_1 to the reactor R. By switching valve V_R, the reaction mixture could bypass the reactor for analysis. The flow-rates of the two gases in the mixture were controlled with flow controllers. On/off valves allowed each gas line to be preferentially selected.

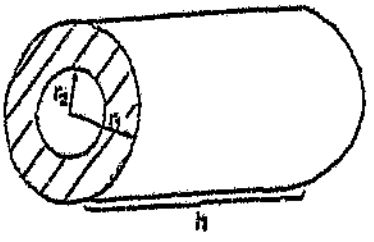


Figure 2.1 Determination of Vp and Vc (penetration profile) by optical microscopy (28).

Vc = total volume of the catalyst pellet = $\pi r_1^2 h$

where r_1 = radius of pellet

h = length of pellet

Vs = volume of support not plated = $\pi r_2^2 h$

where r_2 = radius of area not plated (i.e. inner core)

Vp = volume of peel containing plated Co = Vc - Vs

= $\pi h(r_1^2 - r_2^2)$

2.3 Apparatus used.

During the plating process, the plating solution was stirred continuously to ensure proper mixing of the solution while the plating process was in progress. Measurement and adjustment of pH and temperature had to take place simultaneously. For this purpose, a magnetic stirrer with heating ability was used, while the pH electrode as well as the electronic thermometer was placed well below the surface of the plating solution. The following apparatus was used:

1) **pH meter and electrode:**

   Knick model 761 Calimatic, with pH combination electrode No. N 6280 with built-in temperature compensation.

2) **Hot plate stirrer:**

   Corning model PC 351.

3) **Electronic thermometer:**

   Minitherm HI 8053: Hanna Instruments, -10 °C - 100 °C.

2.4 Characterization of supported catalysts.

2.4.1 Optical microscopy.

Optical microscopy was used for the determination of the degree of penetration of the catalyst into the support, and thus the Vp/Vc ratios. A NIKON Phase Contrast microscope at a magnification setting of 100x, fitted with a calibrated vernier scale, was used to measure the respective dimensions of the plated and non-plated sections of the support pellets, as illustrated in figure 2.1. From these, the Vp/Vc ratios were calculated.

2.2.1 Support used.

The same support was used as for the electroless plating of cobalt (2.1.1), i.e. product designation AL-0104 T Lot no. H328.

2.2.2 Activation treatment of support.

The same procedure was followed as for the electroless plating of cobalt (2.1.2)

2.2.3 Plating procedure.

The plating conditions were varied according to the variable being studied. After numerous trial runs, it was decided to adopt the following basic procedure:

1) The plating bath used would be as in table 2.4 (Formulation 1).
2) The plating time would be 10 minutes.
3) The temperature of the plating bath would be 60 °C.
4) A volume of 2 ml. of plating solution would be used for every pellet being plated.
5) After plating, pellets would be removed and washed in distilled water until all visible traces of plating solution were removed.
6) Pellets would then be washed with distilled water four times, at ten minute intervals, and left overnight in the last volume of distilled water.
7) After 24 hours, all pellets would again be rinsed in distilled water four times.
8) Pellets would then be left on filter paper to air dry for 24 hours, before being dried in a forced circulation oven at 90 °C for another 24 hours.
9) Pellets were then stored in air-tight glass containers until needed.

Table 2.4 Bath formulations for electroless gold plating, from patent literature (8).

Bath constituents.	1	2
Potassium gold cyanide. $KAu(CN)_2$	0,005 mol/l	0,005 mol/l
Dimethyl amine borane. $C_2H_{10}BN$	0,05 mol/l	0,05 mol/l
Potassium hydroxide. KOH	0,8 mol/l	0,8 mol/l
Potassium cyanide. KCN	0,035 mol/l	0,035 mol/l
Potassium carbonate. K_2CO_3	1,0 mol/l	0,45 mol/l
Lead acetate. $Pb(CH_3COO)_2$	15 mg/l	15 mg/l
Hydrazine hydrate.	---	0,25 mol/l

It was mentioned by Pearlstein that dense gold deposits were produced on gold, silver, palladium, platinum and copper with the formulation mentioned in table 2.3.

It was decided to use formulation no. 1 from the patent literature (Table 2.4), as a basic formulation for the evaluation of electroless plating on alumina. The formulation given by Pearlstein in table 2.3 was never evaluated, because of the unavailability of potassium borohydride at the time.

2.2. Bath preparation: electroless gold plating.

A number of electroless gold plating baths have been described in the technical and patent literature (8,9). According to Pearlstein, there is reason to believe that the baths functioned predominantly by electrochemical displacement, rather than by autocatalytic mechanism, or that they had impractically low deposition rates.

A typical bath composition given by Pearlstein is shown in table 2.3.

Table 2.3 A typical bath composition for electroless gold plating, given by Pearlstein (8).

Bath constituents	Concentration
Potassium gold cyanide. $KAu(CN)_2$	5,8 g/l
Potassium cyanide. KCN	13,0 g/l
Potassium hydroxide. KOH	11,2 g/l
Potassium borohydride. KBH_4	21,6 g/l
Temperature	75 °C

Two more formulations obtained from the patent literature are listed in table 2.4. Excellent stability as well as high plating rates for these formulations were claimed, apparently because of the addition of a carbonate compound which accelerated the oxidation kinetics of the reducing agent on gold substrates without affecting the agents present to maintain bath stability. It was also claimed that gold could be plated from these baths for at least six days without apparent bath deterioration (8).

2.1.3 Plating procedure.

The plating conditions were varied according to the variable studied. After numerous trial runs, it was decided to adopt the following basic procedure:

1) The plating bath used would be as in table 2.2.
2) The plating time would be 10 minutes.
3) The temperature of the plating bath would be 60 °C.
4) The pH of the plating bath would be maintained at 8,00.
5) A volume of 2 ml. of plating solution would be used for every pellet being plated.
6) After plating took place, pellets would be removed and washed in distilled water until all visible traces of plating solution were removed.
7) Pellets would then be washed with distilled water four times, at ten minute intervals.
8) Pellets would be left overnight in a volume of distilled water, as described in 7) above.
9) After 24 hours, all pellets would again be rinsed in distilled water four times.
10) Pellets would then be left on filter paper to air dry for 24 hours, before being dried in a forced circulation oven at 90 °C for another 24 hours.
11) Pellets would then be stored in air-tight glass containers until needed.

2.1.1 Support used.

Alumina was used as support throughout, supplied by Engelhard de Meern D.V., Chemical Catalyst Division, The Netherlands.

The support was in the form of cylindrical pellets, with a length of 3,4 mm, a diameter of 3,2 mm and a surface area of 170 m^2/g. Product designation was Al-0104 T, Lot no. H328.

2.1.2 Activation treatment of support.

The electroless plating technique permits metal plating on non-conducting materials such as alumina, once the surface has been made catalytic by a suitable activation treatment. To achieve this, the pellets were soaked in a solution containing palladium nitrate. The procedure was as follows:

1) The required number of pellets were soaked for 30 minutes in a solution of palladium nitrate, using 1 ml. of a 1 g/l palladium nitrate solution per pellet.
2) The pellets were rinsed four times with distilled water.
3) Pellets were washed in ethanol, at a volume of 1 ml. of ethanol per pellet. Pellets were left to soak for 5 minutes.
4) After soaking in ethanol, pellets were again rinsed four times in distilled water. These were then ready for immersion in the plating solution.

Table 2.2. Basic plating bath formulation as used for all experimental work.

Bath constituents	Concentration, g/l
Cobalt nitrate. $Co(NO_3)_2.6H_2O$	60
Sodium hypophosphite. NaH_2PO_2	20
Sodium citrate. $Na_3C_6H_5O_7.2H_2O$	35
Ammonium nitrate. NH_4NO_3	50

Since electroless cobalt plating with hypophosphite as reducing agent will not occur in acid medium, the pH of the bath had to be adjusted to a basic pH in this work. Since Pearlstein (9) reported that lower deposition rates were obtained when sodium hydroxide was used to adjust the pH, it was decided to use ammonium hydroxide. The plating bath contained a complexing agent to stabilize the solution, which also inhibited the formation of cobalt phosphite precipitates. Because of the sensitivity of this bath to pH, ammonium nitrate was used as a buffering agent to maintain the pH at the desired value.

Table 2.1 Typical compositions for electroless cobalt deposition baths (9).

Bath constituents, g/l	1	2	3	4	5	6
Cobalt chloride. $CoCl_2.6H_2O$	30	30	7,5	27 1	--	--
Cobalt sulphate . $CoSO_4.7H_2O$	--	--	--	--	24	25
Sodium hypophosphite. $NaH_2PO_2.H_2O$	20	20	3,5	9	20	--
Dimethylamine borane. $(CH_3)_2NHBH_3$	--	--	--	--	--	4
Sodium citrate. $Na_3C_6H_5O_7.2H_2O$	84,5	29,6	27,4	90	70	--
Ammonium chloride. NH_4Cl	50	50	12,5	45	--	--
Ammonium sulphate. $(NH_4)_2SO_4$	--	--	--	--	40	--
Sodium lauryl sulphate $C_{12}H_{25}O_4SNa$	--	--	,015	--	0,1	--
Sodium succinate. $C_4H_4Na_2O_4.6H_2O$	--	--	--	--	--	25
Sodium sulphate. Na_2SO_4	--	--	--	--	--	15
pH	9,5	9,5	8,2	8,4	8,5	5,0
Temperature, °C	92	92	80	75	92	70

In this work it was decided to use a formulation similar to formulation no. 2 in taule 2.1, but to use nitrate salts throughout, instead of chloride salts, as described by Pearlstein. This was done with a view to the possible use of the prepared catalyst in the FT-synthesis. Nitrate ions are preferred to chloride ions in the precursor salts used in the synthesis of F-T catalysts, because it is known that chloride ions can poison the F-T catalyst. The bath formulation decided on is shown in table 2.2.

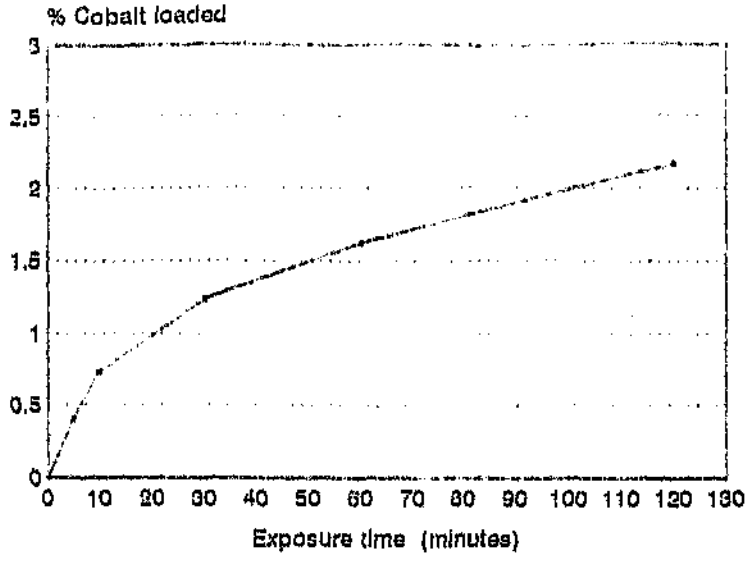


Figure 3.3(a). The effect of variation in exposure time of support pellets on the impregnation of cobalt (%) from a solution containing cobalt nitrate and sodium citrate, in the absence of a surface activation treatment.

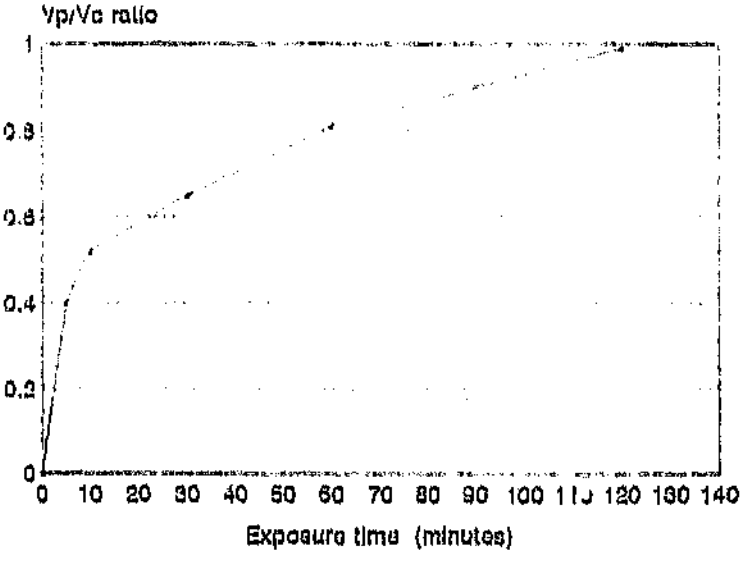


Figure 3.3(b). The effect of variation in exposure time of support pellets on the penetration profile, from a solution containing cobalt nitrate and sodium citrate, in the absence of a surface activation treatment.

3.1.3 Determination of impregnation of cobalt and penetration profile from a solution containing cobalt nitrate and sodium citrate, in the absence of activation treatment.

Support pellets were not subjected to a surface activation treatment, but submerged in a solution containing 60 g/l of cobalt nitrate and 35 g/l sodium citrate at 60 °C. Exposure time was varied between 5 and 120 minutes. In order to compare the results with those obtained in section 3.1.1 and 3.1.2, the pH was adjusted to 6,28 at 60 °C. The data obtained are listed in table 3.3 and shown in figures 3.3(a) and (b).

Table 3.3 The effect of variation in exposure time from a solution containing cobalt nitrate and sodium citrate, in the absence of a surface activation treatment.

EXPOSURE TIME, minutes,	Vp/Vc RATIO	COBALT LOADED, %
5	0,40	0,40
10	0,52	0,73
30	0,65	1,24
60	0,81	1,62
120	0,99	2,17

In this case, it was possible to measure the extent of penetration of the metal by optical microscopy, because of the much higher metal loadings obtained.

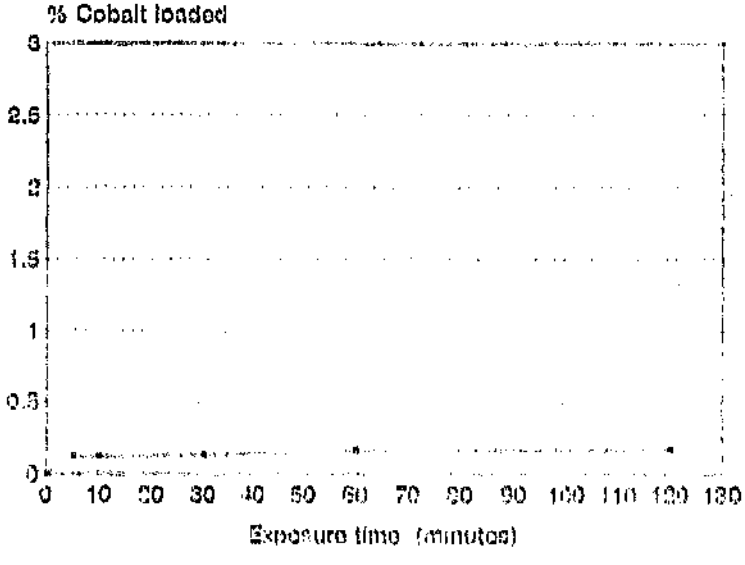


Figure 3.2 The effect of the variation in exposure time of support pellets on the impregnation of cobalt (%) from a cobalt nitrate solution, in the presence of a surface activation treatment.

3.1.2 Determination of impregnation of cobalt from a solution containing only cobalt nitrate, in the presence of a surface activation treatment.

Support pellets were subjected to a surface activation treatment which involved adding the pellets to a solution containing 1 g/l palladium nitrate at a pH of 2,00 for 30 minutes. The support pellets were then submerged into a solution containing only 60 g/l of cobalt nitrate, at 60 °C, and the exposure time was varied between 5 and 120 minutes. The pH of the cobalt nitrate solution was 7,04 at 20 °C, and 6,28 at 60 °C. The pH of the plating solution was not adjusted. The data obtained are listed in table 3.2 and shown in figure 3.2.

Table 3.2 The effect of variation in exposure time from a solution containing only cobalt nitrate, in the presence of a surface activation treatment.

EXPOSURE TIME, minutes.	COBALT LOADED, %
5	0,12
10	0,12
30	0,13
60	0,16
120	0,17

As in 3.1.1, it was not possible to measure the extent of penetration of the metal by optical microscopy, because of the very low metal loadings obtained.

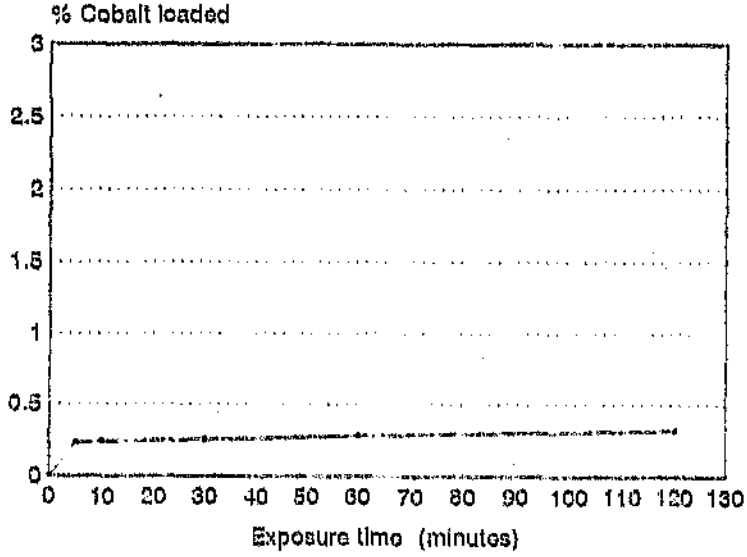


Figure 3.1. The effect of the variation in exposure time of support pellets on the impregnation of cobalt (%) from a cobalt nitrate solution, in the absence of surface activation treatment.

3.1.1 Determination of impregnation of cobalt from a solution containing only cobalt nitrate, in the absence of a surface activation treatment.

Support pellets were submerged into a solution containing only 60 g/l of cobalt nitrate, at 60 °C. No surface activation treatment was used. The pH of the cobalt nitrate solution was 7,04 at 20 °C, and 6,28 at 60 °C. No adjustment was made to the pH of the plating solution, because of the formation of a precipitate of possibly the hydroxide, under alkaline conditions. The time of exposure was varied between 5 and 120 minutes. The procedure described in section 2.3.3. was followed. The data obtained are listed in table 3.1. and shown in figure 3.1.

Table 3.1 The effect of variation in exposure time from a solution containing only cobalt nitrate, in the absence of a surface activation treatment.

EXPOSURE TIME, minutes.	COBALT LOADED,%
5	0,23
10	0,24
30	0,25
60	0,28
120	0,32

It was not possible to calculate the Vp/Vc ratio of the above samples. The layer of metal rendered onto the support, as a result of the low cobalt loadings, could not be distinguished from the background colour of the pellet by optical microscopy.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 RESULTS: ELECTROLESS PLATING OF COBALT ON ALUMINA

The electroless plating technique entails the use of numerous reagents and a range of reaction variables (temperature, concentration etc.) to bring about the deposition of the required metal on a support.

In order to establish the influence of the reagents and each variable, a range of experiments were performed. These were carried out in the following sequence:

1) A reference for the evaluation of the metal loadings was obtained for the electroless plating procedure by determining the metal loadings obtained by impregnating the support with a solution containing the same concentration of cobalt metal as was used in the plating baths. This was done at the same temperature as used for the actual plating baths, namely 60 °C. The impregnation was done in the absence as well as in the presence of the activation treatment required in the electroless plating process.

2) The influence of the initiating surface treatment with palladium nitrate was determined. The data were compared with results obtained without any surface treatment. The effect of pH of the surface treatment was also investigated.

3) The effect of the reducing agent used in the plating bath, both in the absence as well as in the presence of the above surface activation treatment, was determined.

4) The effect of the stabilizer, sodium citrate, on the plating process was determined.

5) The effects of variation in pH, temperature, metal concentration of the plating bath, and plating time, on the percentage cobalt loaded, were determined.

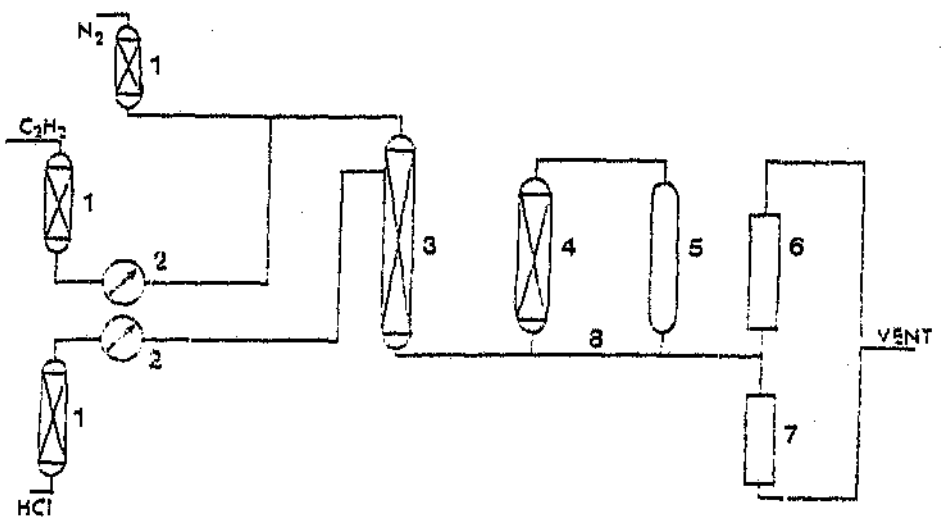


Figure 2.4 Laboratory micro-reactor used for catalyst testing: 1, drying column; 2, rotameter; 3, flash arrestor; 4, mixer; 5, preheater; 6, reactor; 7, sodium hydroxide traps; 8, flowmeter (22).

The experimental procedure was relatively simple, due to the programmable integrator and multi-ramping temperature controllers.

During this time the reactor was programmed. The integrator was programmed to switch the sampling valves to the sampling position at time zero. At the same time, the signals from both the FID and TCD were recorded. The FID signal was plotted. Ten minutes were allowed to completely flush the sampling valves, which were then switched to the collecting position. After 28 minutes the integrator stopped collecting data and reported the integrated peak areas and retention times. The reactor was then reset to zero and the feed gas was manually switched to bypass the reactor. The reactor was removed once it had cooled and was cleaned.

2.5.2 Hydrochlorination of acetylene.

The installation used for conducting the catalytic studies is shown in figure 2.4.

Experiments were conducted at atmospheric pressure using a pyrex reactor. Acetylene was passed through 13X molecular sieve to remove traces of acetone and moisture. Hydrogen chloride gas was similarly dried using 3A molecular sieve. Gas flow-rates were controlled using calibrated rotameters. The dried gases were then mixed, preheated to 180 °C and passed over the catalyst. Product gases were then analysed by gas chromatography.

detected because of hydrogen being the carrier gas, a thermal conductivity detector was used. In order to be able to detect nitrogen, argon was used as carrier gas for the TCD instead of nitrogen. At 35°C, separation of hydrogen and nitrogen was achieved.

Plated pellets were ground with a mortar and pestle to a fine consistency, then pressed in a die by an industrial press into a solid pellet at a pressure of 5 ton. This solid pellet was then again ground, and sieved to maintain the fraction between 300 and 500 microns. This fraction was used in the reactor study.

After weighing out 0,1000 g of catalyst, it was poured into the reactor and tapped down to uniformly cover the quartz bead support bed. The reactor was then secured inside the heating jacket.

Hydrogen gas was directed through the reactor using the three-way valve, while the oxygen flow was switched off. The heating jacket temperature controller was programmed to heat the reactor to 200°C and to maintain this for 5 minutes, then to heat the reactor to 600°C and to maintain this for 30 minutes to allow the reaction system to equilibrate. The sample valves were positioned such that the product stream was routed through the sample loops. When the sample valves were switched to the "sample" position, the gas in the sample loops represented the steady state product gas of the reactor at 600°C.

The reactor jacket temperature was controlled by a multi-ramping temperature controller, and measured by a thermocouple placed inside the jacket, but outside the reactor. It was assumed that the hottest zone of the jacket would be at the centre, and the reactor was placed so that the position of the catalyst bed coincided with the middle of the heating jacket. Every effort was made to ensure that the thermocouple was replaced in exactly the same position for consecutive experiments, although it was not possible to be sure of its exact repositioning after removal.

High gas flow-rates were desirable to minimize gas phase reactions, which meant small contact times. This was achieved by setting the mass flow controllers on the air and methane lines to give flow-rates of 428 cm^3/min and 180 cm^3/min respectively. It was assumed that air contains 21% oxygen, therefore the ratio of methane:oxygen was 2:1.

2.5.1.2 Analysis.

Two different detectors were used for the analysis of the product. A thermal conductivity detector (TCD), which detects differences between the thermal conductivity of the product gas and a reference stream of the carrier gas, and a flame ionisation detector, which measures the heat of combustion of the products in air.

The presence of a NiO_2/Al_2O_3 catalyst in this installation converted all carbon-containing compounds in the presence of excess hydrogen to methane, which was the only carbon-containing compound ever detected. To detect the hydrogen produced, which could not be

The product gases, after being routed via two pneumatically operated sampling valves S_1 and S_2, were vented to the atmosphere. The sampling valves were connected to the same actuator to allow simultaneous sampling.

A 30ml/min stream of hydrogen, controlled with a flow controller, was used as the carrier gas for the FID. During sample collection, the product gas stream was routed through the sample loop, and the carrier was bypassed. By switching the valve, the carrier gas was rerouted through the sample loop, and the product gases in the sample loop at the time of switching were added to the carrier stream. The sample of product gases were then separated in a 3,0 m Porapak QS column at 60°C, B. The product gases then passed through a 0,8 m column packed with a NiO_2/Al_2O_3 catalyst, heated to 350°C, C. The FID, fuelled by the hydrogen carrier, was operated at 250°C.

The inert feed was split and both streams were routed via pressure controllers. The reference stream flow-rate of 30 ml/min was controlled with a needle valve. The sample stream passed through the sampling valve and the Carbosieve SII column, prior to detection in the TCD. Both the sampling valves, Carbesieve SII column and the TCD were operated at an oven temperature of 35°C.

The output signals from the two detectors were collected and integrated on a Varian 4290 integrator. The integrator also controlled the actuator used to control the sampling valves.

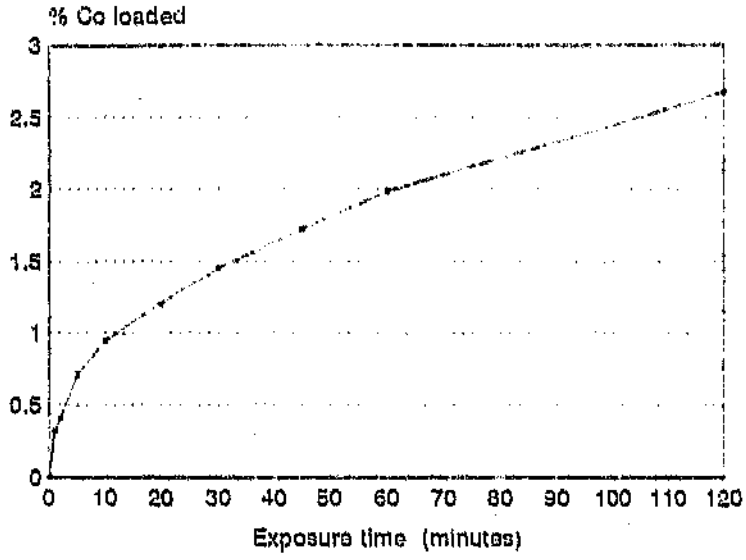


Figure 3.9(a). The effect of variation in exposure time of support pellets on the impregnation of cobalt (%) in the absence of a reducing agent.

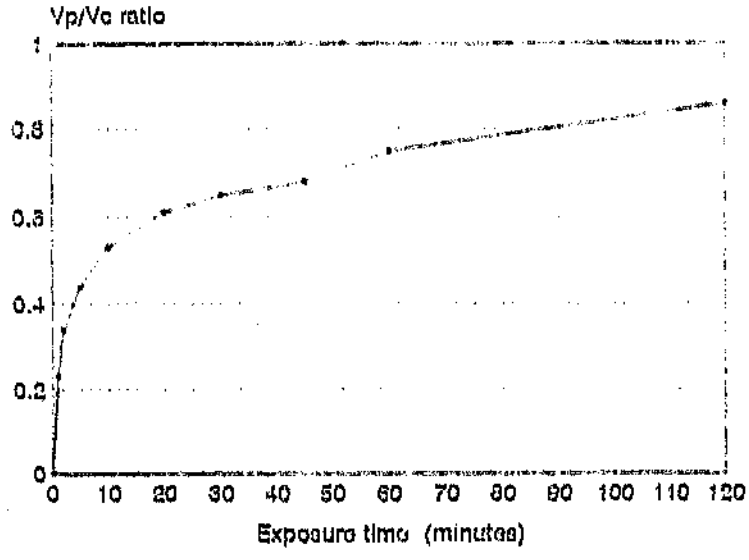


Figure 3.9(b). The effect of variation in exposure time of support pellets on the penetration profile in the absence of a reducing agent.

3.1.9 Determination of the impregnation of cobalt and the penetration profile in the absence of a reducing agent.

A surface activation treatment, consisting of 1 g/l palladium nitrate solution of pH 2,00, was used.The plating bath formulation described in table 2.2. was used, but no reducing agent (sodium hypophosphite) was added to the plating bath. Exposure time was varied between 1 and 120 minutes. The procedure described in section 2.3.3. was followed, and the data obtained are listed in table 3.9 and shown in figures 3.9(a) and (b).

Table 3.9 The effect of variation in support exposure time on the impregnation of cobalt and the penetration profile, in the absence of a reducing agent.

EXPOSURE TIME, minutes.	Vp/Vc RATIO	COBALT LOADED, %
1	0,23	0,32
2	0,34	0,41
5	0,44	0,71
10	0,53	0,94
20	0,61	1,20
30	0,65	1,45
45	0,68	1,72
60	0,75	1,98
120	0,86	2,68

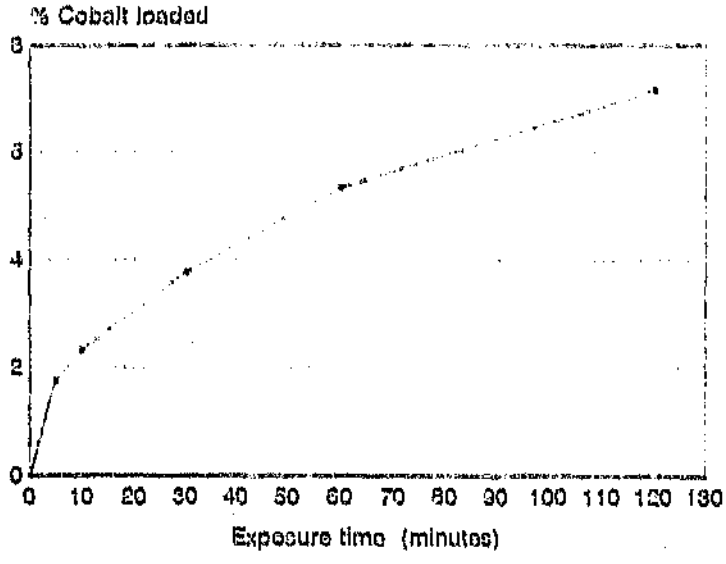


Figure 3.8(a). The effect of variation in exposure tim of support pellets on the impregnation of cobalt (%) in the absence of both an activation treatment and a reducing agent.

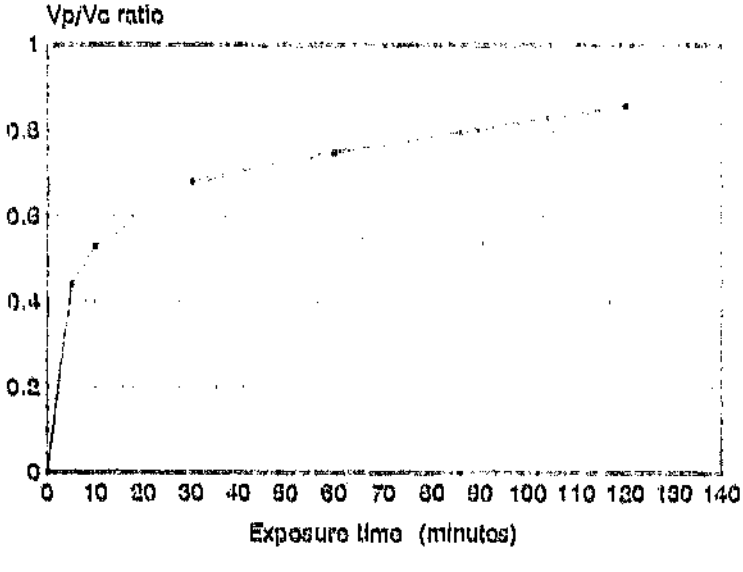


Figure 3.8(b). The effect of variation in exposure time of support pellets on the penetration profile in the absence of both an activation treatment and a reducing agent.

From these results, it can be seen that there is no advantage in using a 2,0 g/l palladium solution instead of a 1,0 g/l solution, since the concentration of palladium in the activation bath has little effect on the subsequent cobalt loading on alumina.

3.1.8 Determination of the impregnation of cobalt and the penetration profile in the absence of both a support activation treatment and a reducing agent.

The support pellets were not subjected to any activation treatment, and the plating bath did not contain the reducing agent, sodium hypophosphite. The pH of the plating bath was adjusted to 8,00. The plating bath formulation described in section 2.2. was used, with the exception of sodium hypophosphite. The procedure described in section 2.3.3. was followed, and the data obtained are listed in table 3.8 and shown in figures 3.8(a) and (b).

Table 3.3 The effect of variation in support exposure time on the impregnation of cobalt and the penetration profile in the absence of both activation treatment and reducing agent.

EXPOSURE TIME, minutes.	Vp/Vc RATIO	COBALT LOADED, %
5	0,44	1,74
10	0,53	2,31
30	0,68	3,76
60	0,75	5,33
120	0,86	7,16

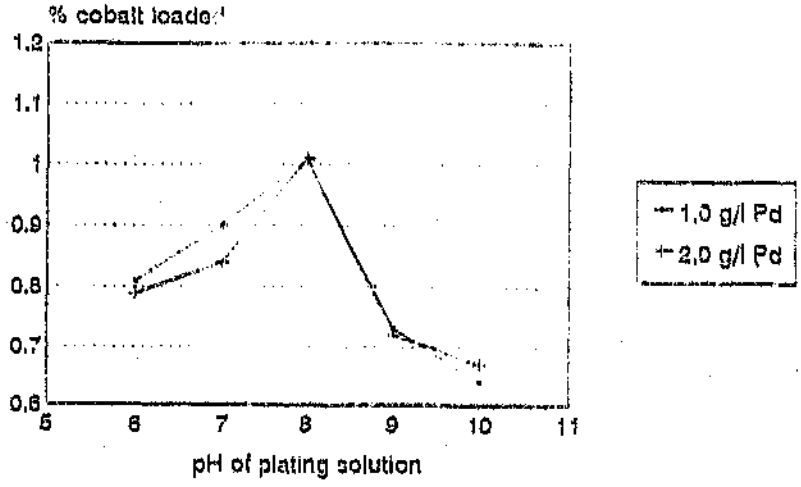


Figure 3.7(a). The effect of variation in concentration of the palladium nitrate surface activation solution of support pellets on the impregnation of cobalt (%) as a function of plating bath pH.

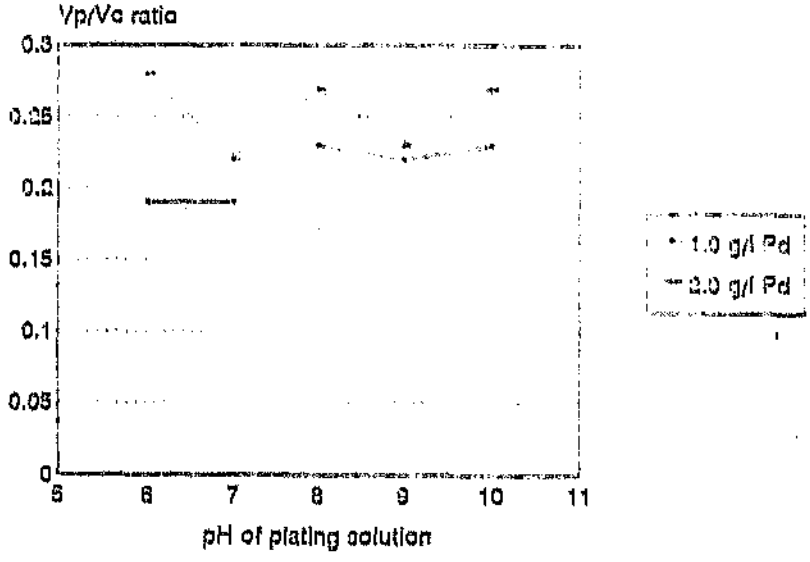


Figure 3.7(b). The effect of variation in concentration of the palladium nitrate surface activation solution of support pellets on the penetration profile as a function of plating bath pH.

The pH of the plating bath was varied between pH 6,00 and pH 9,00 for palladium nitrate concentrations of 1,0 and 2,0 g/l. The plating bath formulation described in table 2.2. was used, except for the pH of the plating bath and palladium concentration of the activation treatment. Plating time was kept constant at 10 minutes. The procedure listed in section 2.3.3 was followed. The data obtained are listed in table 3.7(a) and (b), and shown in figures 3.7(a) and (b).

Table 3.7(a) Penetration profile and impregnation of cobalt at a palladium nitrate concentration of 1,0 g/l.

1,0 g/l $Pd(NO_3)_2$ solution		
pH OF PLATING SOLUTION	Vp/Vc RATIO	COBALT LOADED, %
6,00	0,19	0,81
7,00	0,19	0,90
8,00	0,23	1,01
9,00	0,22	0,73
10,00	0,23	0,64

Table 3.7(b) Penetration profile and impregnation of cobalt at a palladium nitrate concentration of 2,0 g/l.

2,0 g/l $Pd(NO_3)_2$ solution		
pH OF PLATING SOLUTION	Vp/Vc RATIO	COBALT LOADED, %
6,00	0,28	0,79
7,00	0,22	0,84
8,00	0,27	1,01
9,00	0,23	0,72
10,00	0,27	0,57

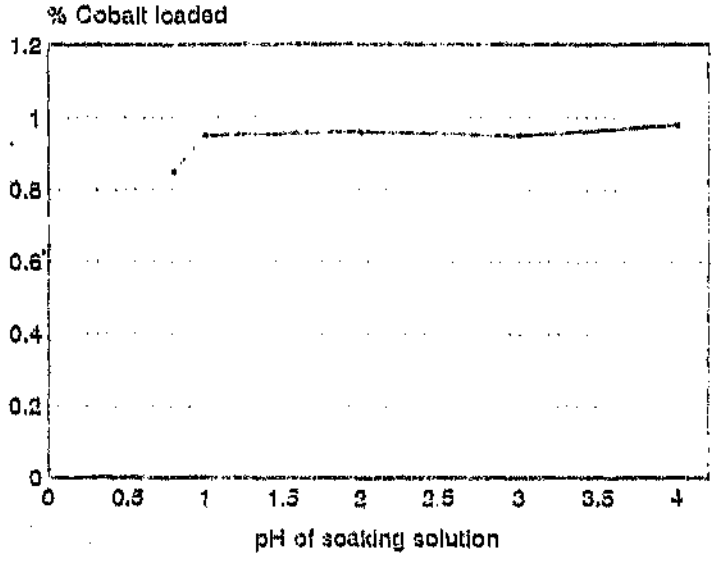


Figure 3.6(a). The effect of variation in pH of the palladium activation treatment of support pellets on the impregnation of cobalt (%).

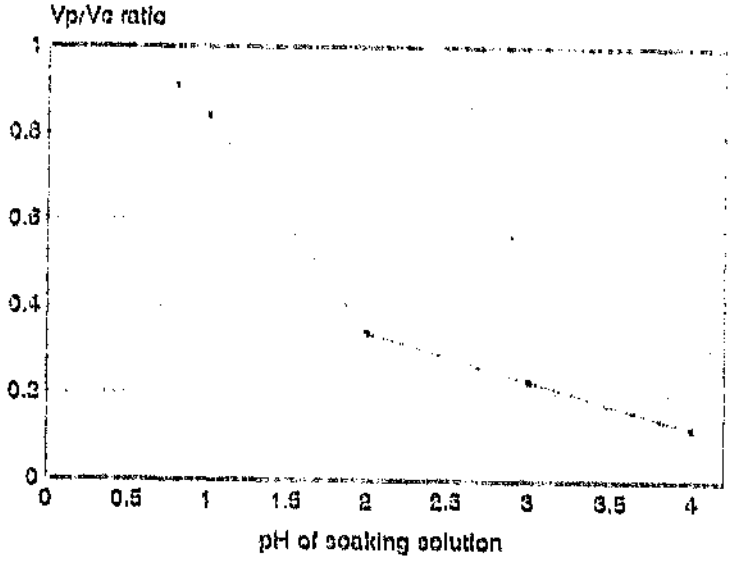


Figure 3.6(b). The effect of variation in pH of the palladium activation treatment of support pellets on the penetration profile.

Table 3.6 The effect of variation of pH of the palladium activation treatment of support pellets.

pH OF PALLADIUM SOAKING SOLUTION	Vp/Vc RATIO	COBALT LOADED, %
0,80	0,91	0,85
1,00	0,84	0,95
2,00	0,34	0,96
3,00	0,23	0,95
4,00	0,12	0,98

3.1.7 Determination of the effect of variation of the palladium concentration of the surface activation treatment and plating bath pH on the impregnation of cobalt and the penetration profile.

An attempt was made to assess the effect of the palladium concentration used for the activation treatment under constant reaction conditions on the penetration profile and the % cobalt loaded onto the support.

Variation of the pH of the activation treatment solution between pH 1 and pH 4 (section 3.1.5.) revealed that the metal loading (ca. 1 %) hardly varied with variation in pH of the activation solution. However to observe a Vp/Vc ratio of about 0,5 a soaking solution with a pH of about 1,5 would be needed. Since the electrode used for measuring pH was designed to be used above pH 2,00 it was decided to use a palladium soaking solution of pH 2,80 for this study which would give a Vp/Vc ratio of about 0,2. At this pH, no visible palladium precipitate was present.

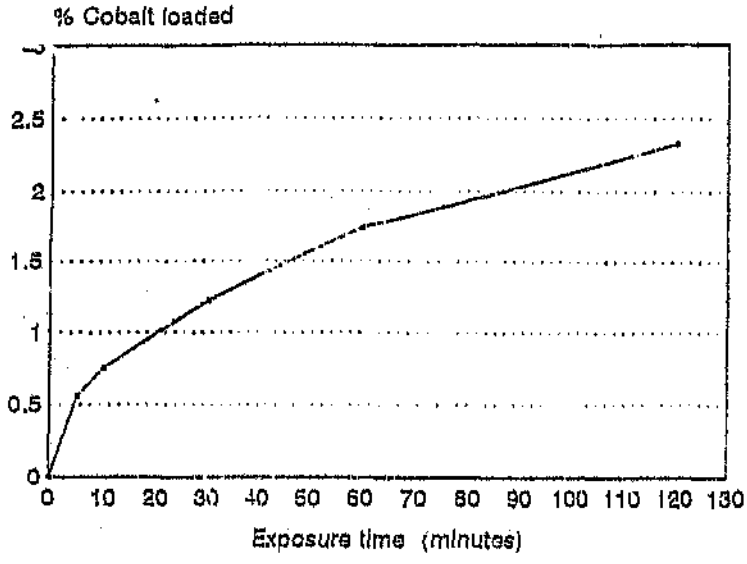


Figure 3.5(a). The effect of variation in exposure time of support pellets on the impregnation of cobalt (%) after support activation with nitric acid (pH 2,00).

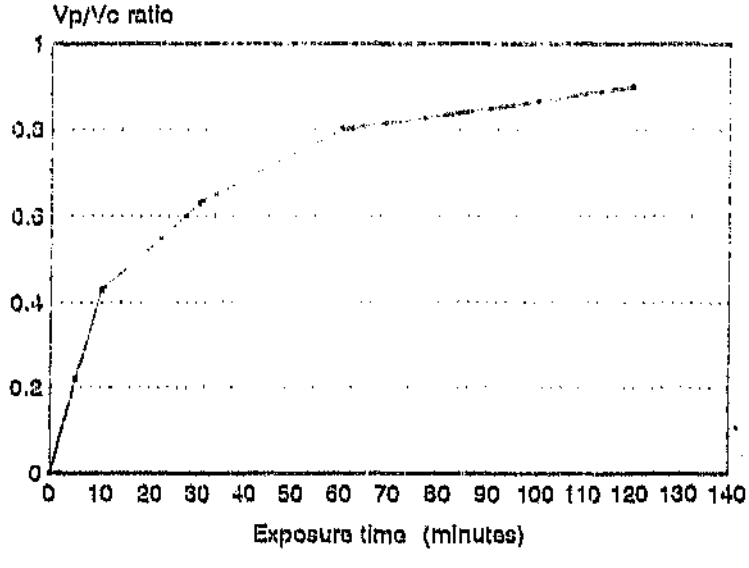


Figure 3.5(b). The effect of variation in exposure time of support pellets on the penetration profile after support activation with nitric acid (pH 2,00).

Table 3.5 The effect of variation in support plating time in the presence of a surface activation treatment consisting of dilute nitric acid of pH 2,00.

EXPOSURE TIME, minutes.	Vp/Vc RATIO	COBALT LOADED, %
5	0,22	0,56
10	0,43	0,76
30	0,63	1,22
60	0,80	1,74
120	0,90	2,33

3.1.6 Determination of the influence of the pH of the activation treatment of support pellets on the impregnation of cobalt and the penetration profile.

The plating bath formulation described in table 2.2. was used, but with the pH of the palladium soaking solution as a variable. The pH after dissolution of palladium nitrate in a small volume of water containing 10 ml. of nitric acid, was between 0,7 and 0,8. The pH of this solution was increased from 0,8 in increments of 1 pH-unit.

Above a pH of about 4,00 it was observed that palladium precipitated from the solution, possibly as an hydroxide, and it was therefore decided to study the influence of the pH of the soaking solution only between pH 0,8 and 4,00 although a slight precipitate was already present at pH 4,00. Plating time was kept constant at 10 minutes. The procedure listed in section 2.3.3 was followed. The data obtained are listed in table 3.6 and shown in figures 3.6(a) and (b).

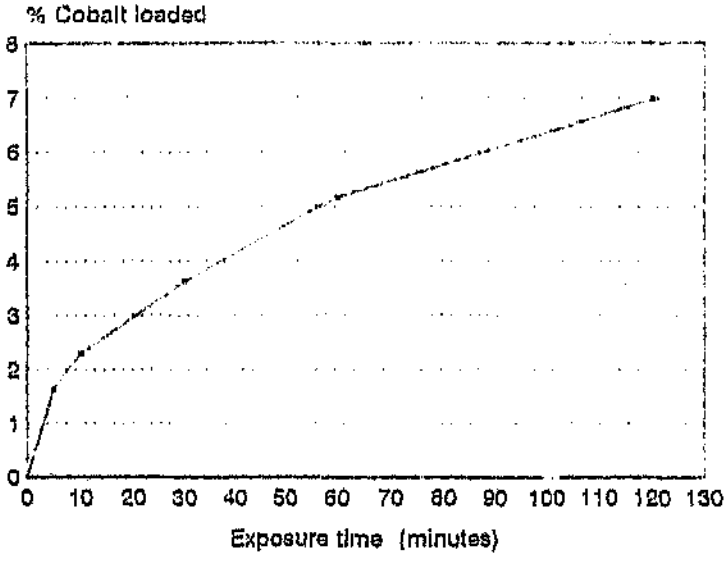


Figure 3.4(a). The effect of variation in exposure time of support pellets on the impregnation of cobalt (%) in the absence of a surface activation treatment.

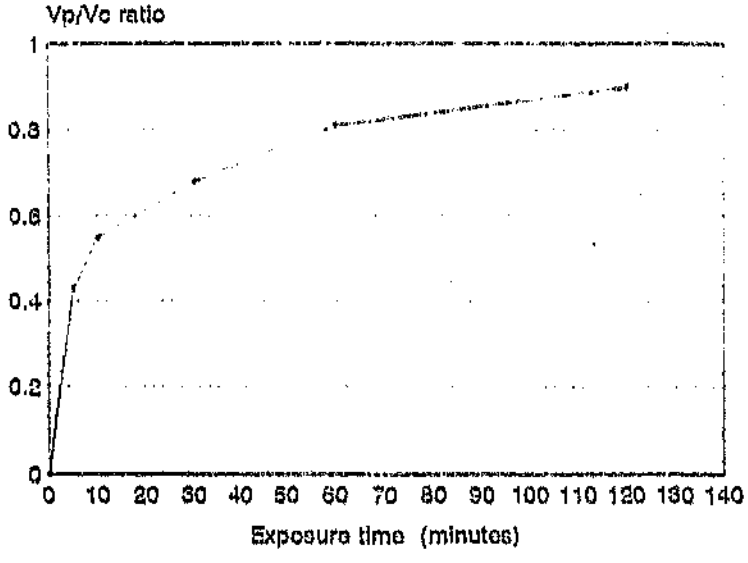


Figure 3.4(b). The effect of variation in exposure time of support pellets on the penetration profile in the absence of a surface activation treatment.

3.1.4 Determination of impregnation of cobalt and penetration profile in the absence of a surface activation treatment, after exposure to all plating reagents.

No pre-activation of the support was attempted. The plating bath formulation described in table 2.2 was used. The procedure described in section 2.3.3. was followed.

The bath temperature was 60 °C, pH of the plating bath was 8,00, and the exposure time was varied between 5 and 120 minutes. The data obtained are listed in table 3.4 and shown in figures 3.4(a) and (b).

Table 3.4 The effect of variation in support exposure time, in the absence of an activation treatment, after exposure to all plating reagents.

EXPOSURE TIME, minutes.	Vp/Vc RATIO	METAL LOADED, %
5	0,43	1,63
10	0,55	2,29
30	0,68	3,63
60	0,81	5,16
120	0,90	6,97

3.1.5 Determination of impregnation of cobalt (all plating reagents) after surface activation treatment of the support at pH 2,00 in the absence of palladium nitrate.

After support pre-treatment with a nitric acid solution of pH 2,00 instead of palladium nitrate, the plating bath formulation described in table 2.2. was used, and the procedure described in section 2.3.3. was followed. The pH of the plating solution was maintained at pH 8,00 and the temperature of the plating bath at 60 °C. Support plating time was varied between 5 and 120 minutes. The data obtained are listed in table 3.5 and shown in figures 3.5(a) and (b).

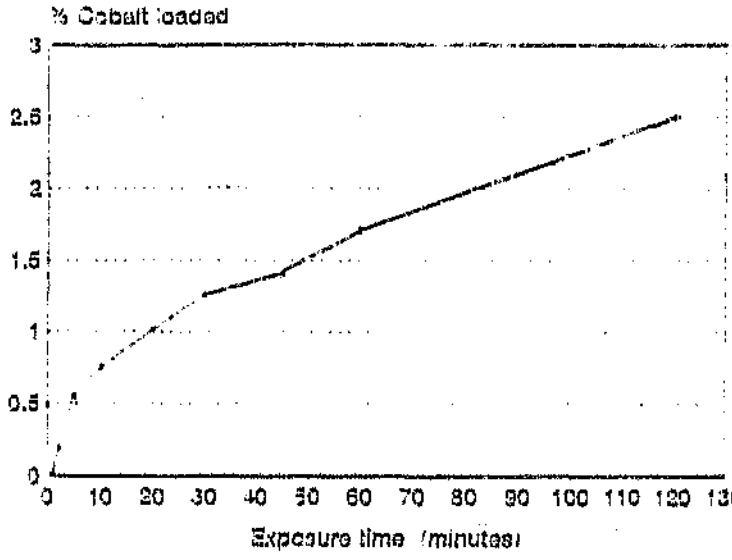


Figure 3.15(a). The effect of variation in support plating time on the impregnation of cobalt (%).

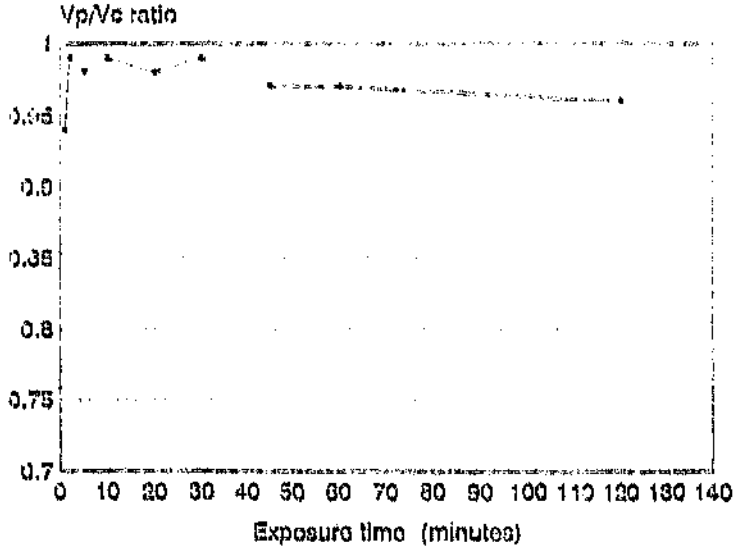


Figure 3.15(b). The effect of variation in support plating time on the penetration profile.

that, when the pH of the plating bath was maintained at 8,00 a precipitate started to form when the cobaltous nitrate concentration exceeded 60 g/l. It is also shown that the penetration profile is not influenced by the variation in cobalt concentration.

3.1.15 Determination of the effect of variation in support exposure time on the impregnation of cobalt and the penetration profile.

A palladium nitrate solution with pH of 0,80 was used in the activation treatment for 30 minutes. Support exposure time was varied between 1 and 120 minutes. Plating bath temperature was maintained at 60 °C, and the pH of the plating bath at 8,00. The plating bath formulation described in table 2.2. was used and the procedure listed in 2.3.3 was followed. The data obtained are listed in table 3.15 and shown in figures 3.15(a) and (b).

Table 3.15 The effect of variation in support exposure time on the impregnation of cobalt and the penetration profile.

EXPOSURE TIME, minutes.	V_D/V_C RATIO	COBALT LOADED, %
1	0,94	0,01
2	0,99	0,19
5	0,98	0,55
10	0,99	0,75
20	0,98	1,01
30	0,99	1,26
45	0,97	1,41
60	0,97	1,74
120	0,96	2,50

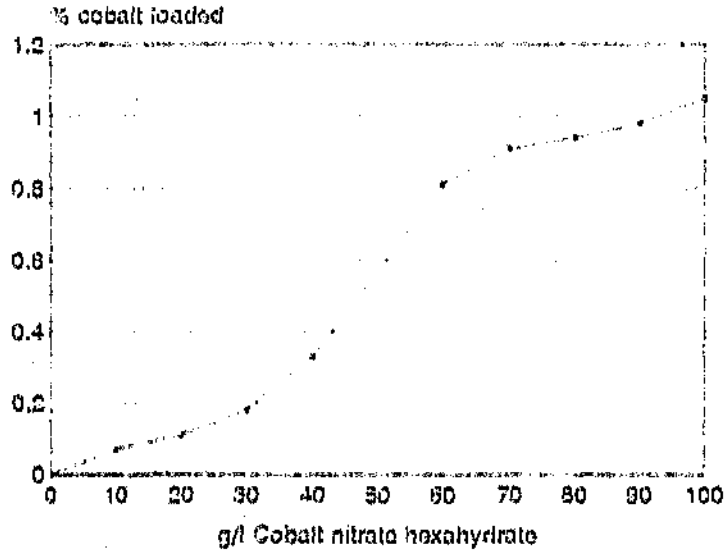


Figure 3.14(a). The effect of variation in cobaltous nitrate concentration of the plating bath on the impregnation of cobalt (%).

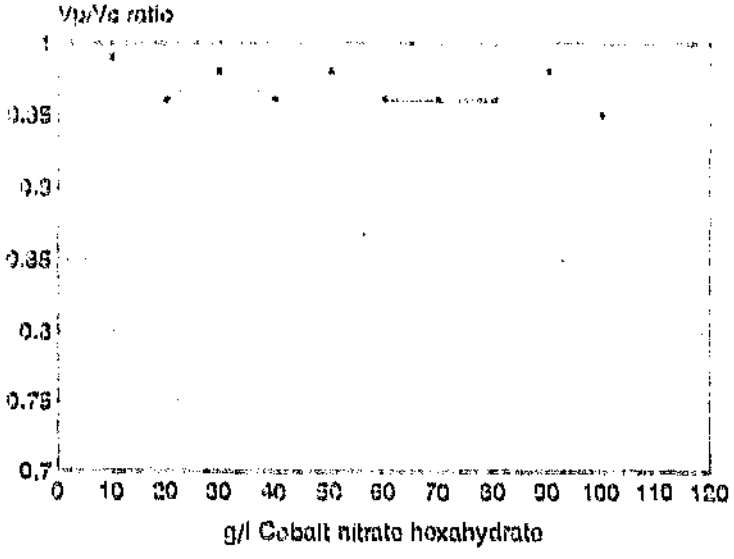


Figure 3.14(b). The effect of variation in cobaltous nitrate concentration of the plating bath on the penetration profile.

3.1.14 Determination of the effect of variation in cobalt concentration of the plating bath on the impregnation of cobalt and the penetration profile.

A surface activation solution, consisting of 1 g/l palladium nitrate at pH 0,80 was used. The plating bath formulation described in table 2.2. was used, and the procedure listed in section 2.3.3. was followed. The cobalt concentration of the plating bath was varied between 10 and 100 g/l of cobaltous nitrate hexahydrate. Exposure time was kept constant at 10 minutes. The data obtained are listed in table 3.14 and shown in figures 3.14(a) and (b).

Table 3.14 The effect of variation in cobaltous nitrate concentration of the plating bath on the impregnation of cobalt and the penetration profile.

COBALTOUS NITRATE CONCENTRATION, g/l	Vp/Vc RATIO	COBALT LOADED, %
10	0,99	0,07
20	0,96	0,11
30	0,98	0,18
40	0,96	0,33
50	0,98	0,60
60	0,96	0,81
70	0,96	0,91
80	0,96	0,94
90	0,98	0,98
100	0,95	1,05

Figure 3.14(a) reveals that the percentage metal loaded increased with an increase in the cobalt content of the plating bath. At concentrations higher than 60 g/l of cobalt nitrate, the rate of increase in % cobalt loaded decreased considerably. It was observed

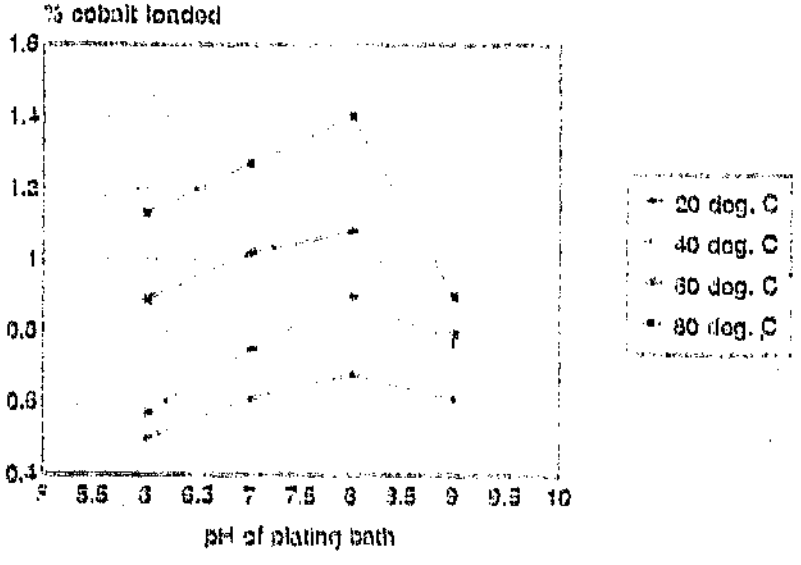


Figure 3.13(a). The effect of variation in temperature and pH of the plating bath on the impregnation of cobalt (%).

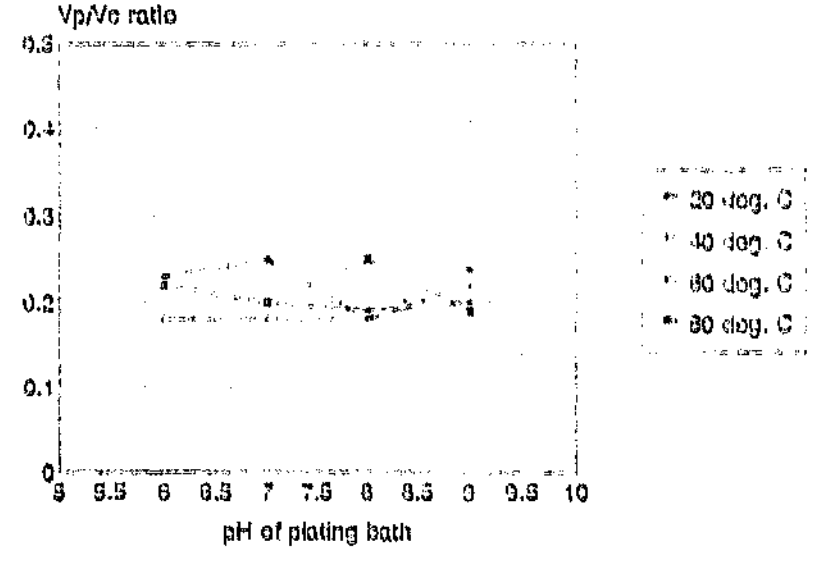


Figure 3.13(b). The effect of variation in temperature and pH of the plating bath on the penetration profile.

Table 3.13 The effect of variation in pH and temperature of the plating bath on the impregnation of cobalt and the penetration profile.

TEMPERATURE, °C	Vp/Vc RATIO	COBALT LOADED, %
pH 6,00		
20	0,22	0,50
40	0,18	0,57
60	0,23	0,89
80	0,22	1,13
pH 7,00		
20	0,20	0,61
40	0,18	0,75
60	0,25	1,02
80	0,20	1,27
pH 8,00		
20	0,19	0,68
40	0,18	0,90
60	0,18	1,08
80	0,25	1,40
pH 9,00		
20	0,20	0,61
40	0,22	0,77
60	0,24	0,79
80	0,19	0,90

From this data, it is clear that the % cobalt loaded onto the support reached a maximum at a pH of 8,00, and that there was a linear response with an increase in temperature from 20 °C to 80 °C at this pH. The penetration profile stayed constant with variation in both temperature and pH of the plating bath.

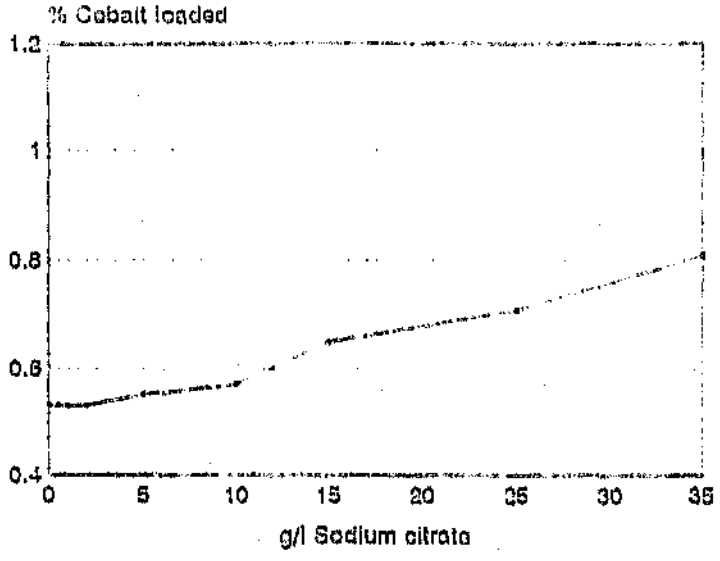


Figure 3.12(a). The effect of variation in sodium citrate concentration of the plating bath on the impregnation of cobalt (%).

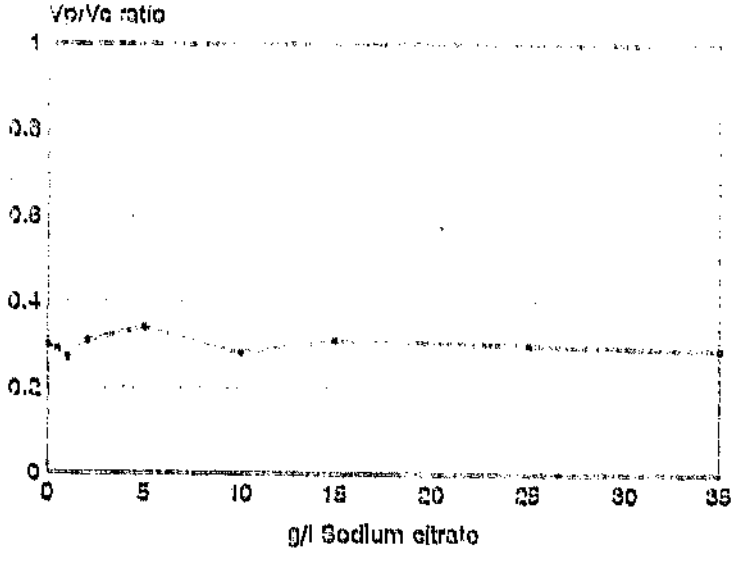


Figure 3.12(b). The effect of variation in sodium citrate concentration of the plating bath on the penetration profile.

The exposure time was kept constant at 10 minutes. and the temperature of the plating bath at 60 °C. The pH of the plating bath was noted before the support pellets were added and after the plating temperature (60 °C) was reached. The procedure described in section 2.3.3. was followed, and the data obtained are listed in table 3.12 and shown in figures 3.12(a) and (b).

Table 3.12 The effect of variation in sodium citrate concentration on the impregnation of cobalt the penetration profile.

SODIUM CITRATE CONCENTRATION, g/l	Vp/Vc RATIO	COBALT LOADED, %	pH OF PLATING BATH
0	0,30	0,53	4,36
0,5	0,29	0,53	4,36
1,0	0,27	0,53	4,38
2,0	0,31	0,53	4,51
5,0	0,34	0,55	4,63
10,0	0,28	0,57	4,67
15,0	0,31	0,65	4,65
25,0	0,30	0,71	4,61
35,0	0,29	0,81	4,65

3.1.13 Determination of the effect of variation in temperature and pH of the plating bath on the impregnation of cobalt and the penetration profile.

The surface activation solution consisted of a palladium nitrate solution with a pH of 2,80. The exposure time was kept constant at 10 minutes. The plating bath formulation described in table 2.2. was used, and the procedure as listed in section 2.3.3 was followed. Both temperature of the plating bath (from 20 °C to 80 °C), and pH of the plating bath (from pH 6,00 to pH 9,00) were varied. The data obtained are listed in table 3.13 and shown in figures 3.13(a) and (b).

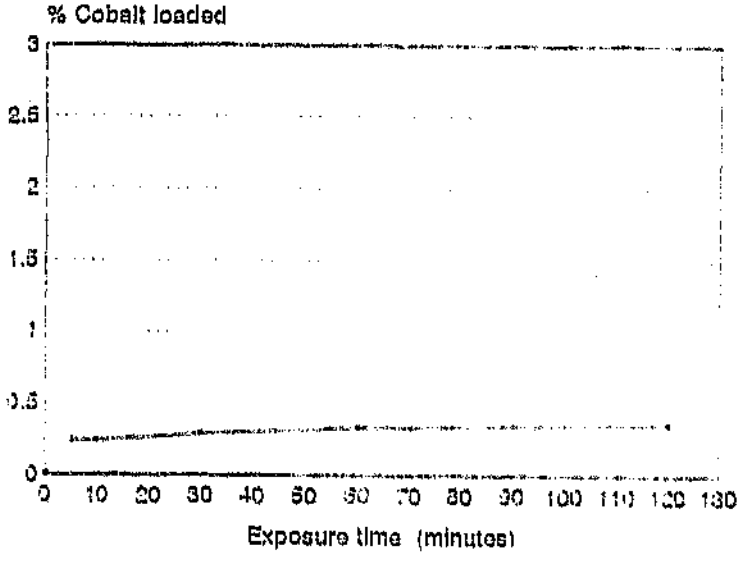


Figure 3.11. The effect of variation in exposure time of support pellets on the impregnation of cobalt (%) in the absence of sodium citrate.

3.1.11 Determination of the effect of variation in support exposure time from a plating bath containing no sodium citrate, on the impregnation of cobalt and the penetration profile.

A surface activation treatment, consisting of 1 g/l palladium nitrate at a pH of 2,00 was used. The plating bath formulation described in table 2.2. was used, but contained no sodium citrate.

The pH of the plating solution was adjusted to 8,00 and the temperature of the plating bath was maintained at 60 °C. Exposure time was varied between 5 and 120 minutes. The data obtained are listed in table 3.11 and shown in figure 3.11.

Table 3.11 The effect of variation in support exposure time from a plating bath containing no sodium citrate, on the impregnation of cobalt and the penetration profile.

EXPOSURE TIME, minutes.	COBALT LOADED, %
5	0,24
10	0,24
30	0,29
60	0,33
120	0,36

As a result of the low cobalt loadings obtained, it was not possible to measure the extent of penetration achieved by the method of optical microscopy.

3.1.12 Determination of the effect of variation in sodium citrate concentration of the plating bath on the impregnation of cobalt and the penetration profile.

A surface activation treatment, consisting of 1 g/l palladium nitrate at a pH of 2,00 was used. The plating bath formulation described in table 2.2. was used, but the concentration of sodium citrate in the plating bath was varied between 0 and 35 g/l.

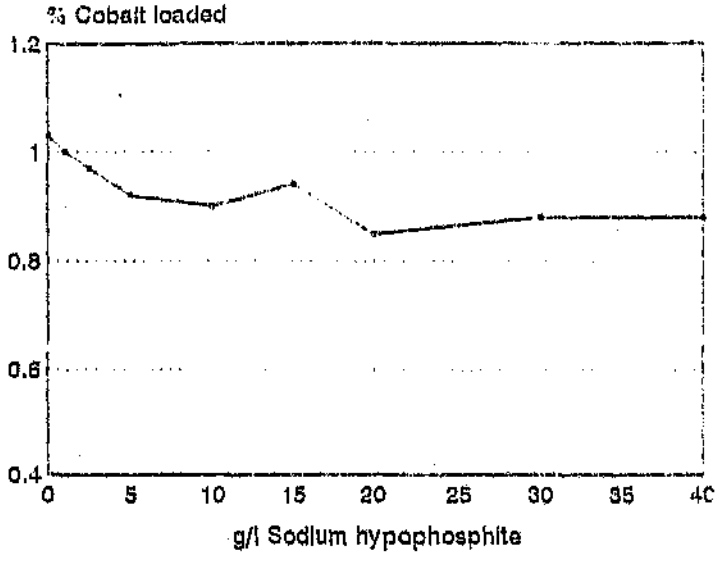


Figure 3.10(a). The effect of variation in sodium hypophosphite concentration of the plating bath on the impregnation of cobalt (%).

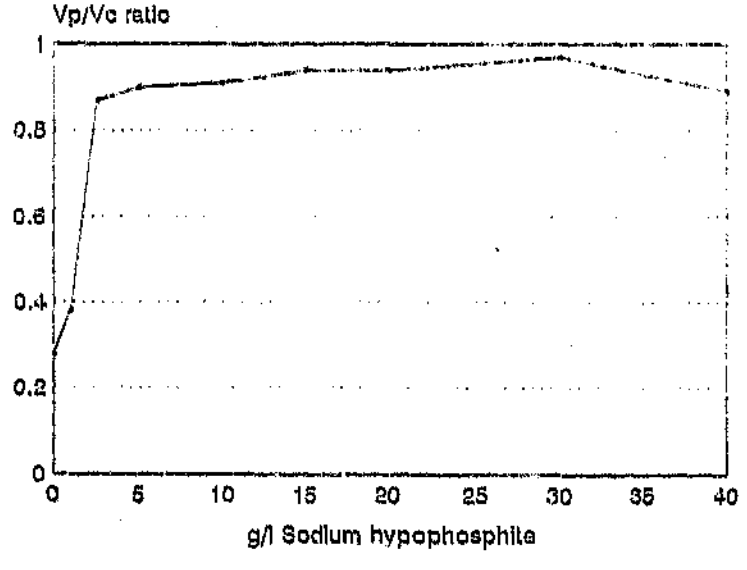


Figure 3.10(b). The effect of variation in sodium hypophosphite concentration of the plating bath on the penetration profile.

3.1.10 Determination of the effect of sodium hypophosphite in the plating bath on the impregnation of cobalt and the penetration profile.

The pH of the palladium nitrate soaking solution was adjusted to 0,80. This was done because the influence of the pH of the surface activation solution has already been established, and it was known not to influence the % metal loaded onto the support. The pH-electrode used for this determination could be used at this pH. The plating bath formulation described in table 2.2. was used, but the sodium hypophosphite concentration was varied between 0 and 40 g/l.

The procedure listed in section 2.3.3 was followed. The plating time was maintained at 10 minutes, the pH of the plating bath at 8,00 and the bath temperature at 60 °C. The data obtained are listed in table 3.10 and shown in figures 3.10 (a) and (b).

Table 3.10 The effect of variation in sodium hypophosphite concentration on the impregnation of cobalt and the penetration profile.

SODIUM HYPOPHOSPHITE CONCENTRATION, g/l	Vp/Vc RATIO	COBALT LOADED, %
0	0,28	1,03
1,0	0,38	1,00
2,5	0,87	0,97
5,0	0,90	0,92
10,0	0,91	0,90
15,0	0,94	0,94
20,0	0,94	0,85
30,0	0,97	0,88
40,0	0,89	0,88

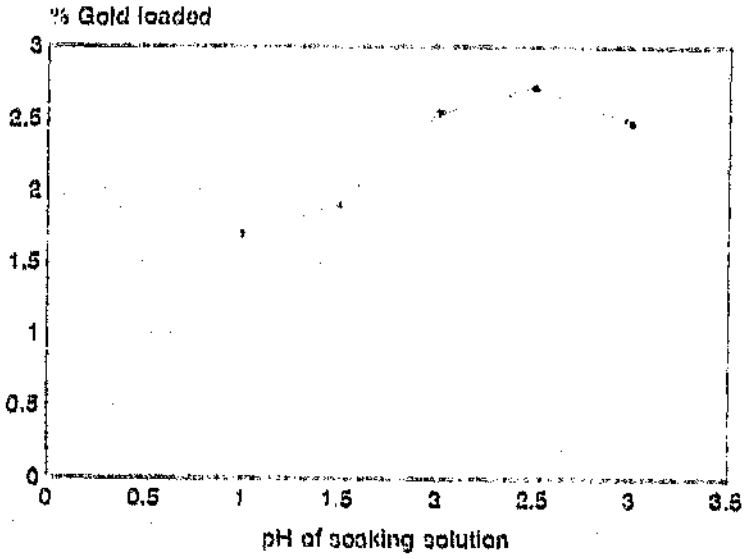


Figure 3.19(a). The effect of variation in pH of the surface activation treatment solution on the impregnation of gold (%).

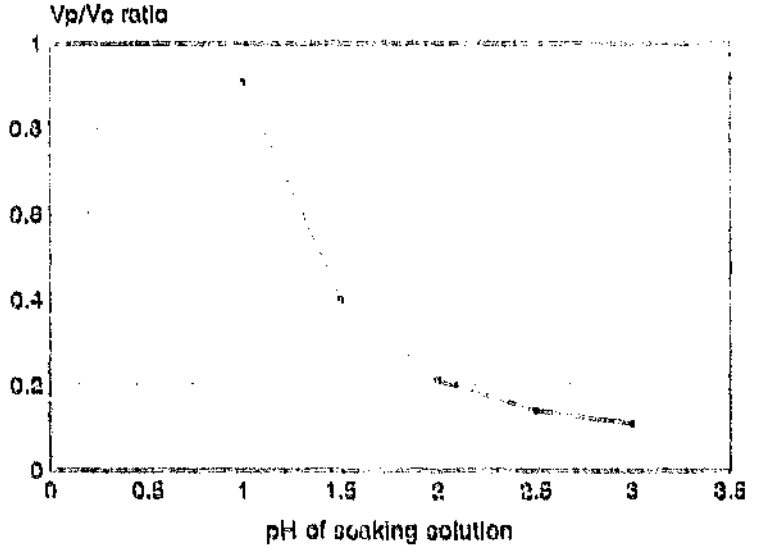


Figure 3.19(b). The effect of variation in pH of the surface activation treatment solution on the penetration profile.

3.3.2 Determination of the effect of variation in temperature of the plating bath on the impregnation of gold and the penetration profile.

The plating bath formulation described in table 2.4 was used, and the procedure described in section 2.4.3. was followed.

The temperature of the plating bath was varied from 25 °C (room temperature) to 80 °C. The pH of the palladium nitrate activation solution was maintained at 2,00. Plating time was 30 minutes. The data obtained are listed in table 3.18 and shown in figures 3.20(a) and (b).

Table 3.18 The effect of variation in temperature of the plating bath on the impregnation of gold and the penetration profile.

TEMPERATURE OF PLATING BATH, °C	Vp/Vc RATIO	GOLD LOADED, %
25°C	0,23	0,23
40°C	0,18	1,04
60°C	0,23	2,70
80°C	0,23	1,87

3.3.3 Determination of the effect of variation in support exposure time on the impregnation of gold and the penetration profile.

The plating bath formulation described in table 2.4 was used, and the procedure described in section 2.4.3. was followed. The temperature of the plating bath was maintained at 60 °C, and the pH of the activation solution at 2,00. Exposure time was varied between 5 minutes and 120 minutes. The data obtained are listed in table 3.19 and shown in figures 3.21(a) and (b).

3.3.1 Determination of the effect of variation in the pH of the activation treatment solution on the impregnation of gold and the penetration profile.

The plating bath formulation described in table 2.4. was used, and the procedure listed in section 2.4.3. was followed. Since it was observed that a palladium precipitate started to form at a pH of about 4,00, it was decided to vary the pH of the activation solution between 1,00 and 3,00. Support exposure time was kept constant at 30 minutes. The data obtained are listed in table 3.17 and shown in figures 3.19(a) and (b).

Table 3.17 The effect of variation in pH of the palladium activation solution on the impregnation of gold and the penetration profile.

pH OF PALLADIUM SOAKING SOLUTION	V_p/V_c RATIO	GOLD LOADED, %
1,00	0,91	1,69
1,50	0,40	1,90
2,00	0,21	2,54
2,50	0,14	2,72
3,00	0,11	2,47

It is shown in table 3.17 that variation in pH of the palladium nitrate solution used in the activation treatment of the support pellets, influenced both the extent of penetration of the catalytic material into the support and the amount of gold loaded.

It can be concluded that it is possible to prepare a supported cobalt catalyst using alumina as support, with any penetration depth desired, and with cobalt loadings of up to 7,50%, using permutations of reaction conditions explored in these sections.

3.3 RESULTS: ELECTROLESS PLATING OF GOLD ON ALUMINA.

The study on cobalt electroless plating provided a basis for understanding and controlling the factors that influence the penetration and loading of a metal. This information provided the basis for a study of gold electroless plating on alumina. Since the key parameters to control the Vp/Vc ratios and metal loadings have been established (section 3.1.), it was only considered necessary to do the following experiments in order to establish precise parameters for the deposition of gold onto alumina.

1) Determination of the optimum pH of the palladium nitrate solution used for the activation treatment of the support pellets.
2) The determination of the optimum temperature, support plating time and potassium hydroxide concentration of the plating bath.
3) The plating bath formulation as mentioned in the literature, contained potassium hydroxide. It was therefore not possible to adjust the pH of the plating bath to the same extent as was possible in the case of the electroless plating bath for cobalt. The presence of potassium cyanide in the bath formulation meant that under acidic conditions, hydrogen cyanide would have been evolved, which would result in the loss of cyanide ions from solution.

3.2.4 The effect of variation in sodium citrate concentration on the impregnation of cobalt.

From the data shown in section 3.1.3, it is clear that in the presence of sodium citrate when no surface activation were employed, much higher metal loadings were obtained. This is significant, since it proved that citrate is indeed critical for an enhanced cobalt uptake by the support in the absence of surface activation.

It was shown in section 3.1.11. that the metal loading obtained in the absence of sodium citrate, varied between 0,24% and 0,36%. At these loadings, the % metal loaded was too low to permit measurement of the penetration profile by optical microscopy. From section 3.1.12, it is clear that the metal loading increased from 0,53 % at 0,5 g/l of sodium citrate, to 0,81% at 35 g/l sodium citrate. It was also observed that the penetration profile was not influenced by variation in sodium citrate concentration, as in the case of variation in sodium hypophosphite concentration. Both sets of experiments were performed after a Pd pre-treatment of the support. Thus the pre-treatment overrides any significant influence of the citrate.

3.2.5 Determination of optimum pH, temperature, cobalt nitrate concentration and plating time.

It was shown in sections 3.1.12 to 3.1.15 that optimum conditions exist for selecting certain metal loadings and penetration depths when preparing supported catalysts. When different palladium concentrations were compared in section 3.1.7, it was shown that in both cases, the Vp/Vc ratio hardly varied. Clearly, the pH of the support activation procedure has the dramatic effect on Vp/Vc ratios.

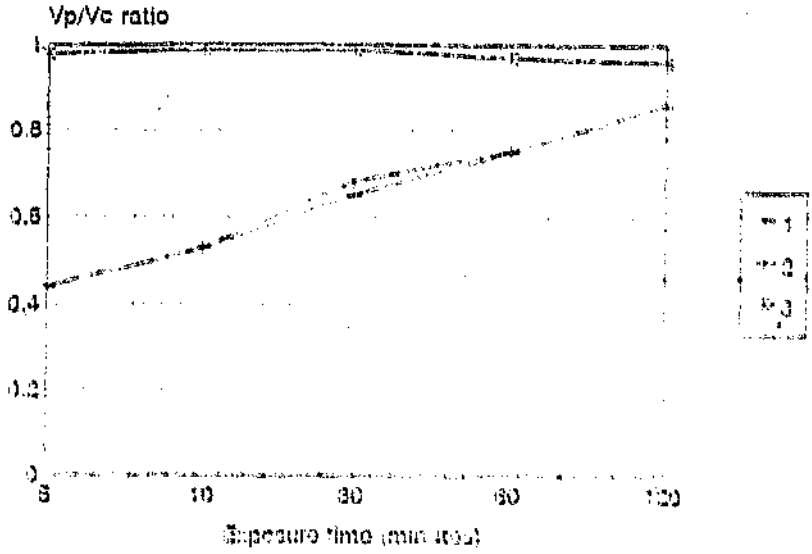


Figure 3.18(b). The effect of sodium hypophosphite as reducing agent on the penetration profile.

1) In the absence of both reducing agent and a surface activator.

2) In the absence of reducing agent, with palladium nitrate (1 g/l, pH 3,00) as surface activator.

3) With sodium hypophosphite as reducing agent, and palladium nitrate (1 g/l, pH 0,80) as surface activator.

It was shown in section 3.1.8 that the penetration profile varied with variation in plating time, in the absence of reducing agent. The same occurrence was observed in section 3.1.9, in spite of the presence of palladium nitrate as surface activation treatment. It is therefore only possible to modify the penetration profile by using palladium nitrate as surface activation treatment when a reducing agent is absent from the plating bath.

The major finding is that a reducing agent actually plays little part in the so-called "plating" process. Thus the whole concept of electroless plating, will need to be considered again in the synthesis of Co/Al_2O_3 catalysts. Indeed it may be that the pre-activation required for the synthesis of cob ' on plastic, for instance, which entails use of $SnCl_4$, may be critical for the plating process.

This is at odds with the preliminary data obtained by Colley earlier in these laboratories (28) and will need to be explored in later studies. What has emerged from these studies is that loading and Vp/Vc ratios can be finely tuned by use of the solution reagents used in the experiments.

Indeed an analysis of the data reveals that neither the pre-activation step with Pd nor the reducing reagent are important variables for obtaining large amounts of Co on the Al_2O_3. If anything they inhibit the loading process. The do however influence the Vp/Vc ratios.

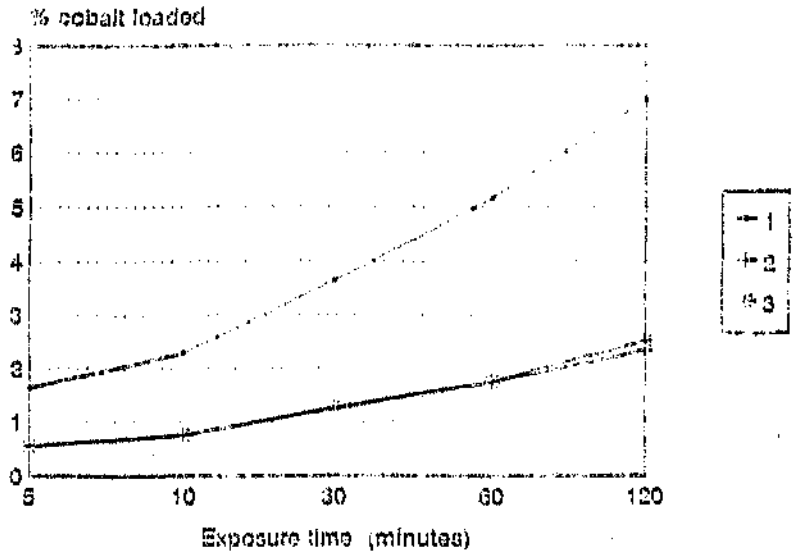


Figure 3.17(a). The effect of different surface activation treatments on the impregnation of cobalt (%).

1) No activation treatment.
2) Nitric acid (pH 2,00) treatment.
3) Palladium nitrate (1 g/l, pH 0,80) treatment.

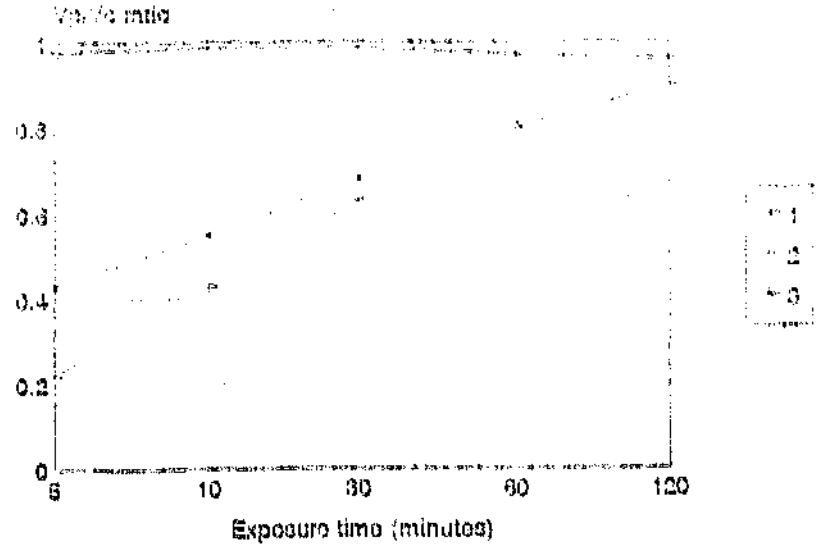


Figure 3.17(b). The effect of different surface activation treatments on the penetration profile.

1) No activation treatment.
2) Nitric acid (pH 2,00) treatment.
3) Palladium nitrate (1 g/l, pH 0,80) treatment.

It can be seen in figure 3.17 that the highest metal loading obtained was for the case where no surface activation treatment was used. It is significant to note that, from the data given above, no advantage is gained from using a surface activation treatment consisting of palladium nitrate when compared to a surface activation treatment with nitric acid (same pH), as far as the % metal loaded is concerned.

It was shown in section 3.1.6. that the depth of penetration is controlled by the pH of the palladium nitrate solution.
This data is consistent with all other experiments carried out in this study. In other words evaluation of all other variables in which the surface activation treatment consisted of use of a solution of palladium nitrate of known pH, provided that the plating bath formulation in table 2.2 was used, always gave the same result.

3.2.3 The effect of the reducing agent on the impregnation of cobalt and the penetration profile.

A comparison of the results obtained in sections 3.1.8, 3.1.9 and 3.1.15 is shown in figure 3.18. In these experiments the role of the hypophosphite reducing agent was explored.

It is shown in figure 3.18 that the highest metal loadings were again obtained from a plating bath where no surface activation treatment was present. In the absence of sodium hypophosphite as reducing agent, it can be seen that the % metal loaded was higher than in the case where reducing agent was present. However the difference was small and invariant with exposure time, although the % difference did vary with time (27% at 5 minutes; 10% at 30 minutes).

3.2.2 Electroless plating of cobalt with different surface activation treatment processes.

A comparison of the results obtained in sections 3.1.4, 3.1.5 and 3.1.15 is shown in figure 3.17. In this series of experiments different surface activation treatments were used (no treatment, nitric acid treatment, Pd activation treatment) followed by use of the same plating bath formulation. Data at a plating time of 10 minutes are compared below in table 3.16.

Table 3.16. Data obtained in sections 3.1.4, 3.1.5 and 3.1.15. Plating time was 10 minutes.

SECTION	COBALT LOADED, %	Vp/Vc RATIO	SURFACE ACTIVATION	pH OF SURFACE ACTIVATION
3.1.4	2,29	0,55	--	--
3.1.5	0,76	0,43	HNO_3	2,00
3.1.15	0,75	0,99	$Pd(NO_3)_2$	0,80

The data suggest that the reagents added to the cobalt nitrate solution have a dramatic effect on cobalt penetration and uptake. Significant, and of concern with respect to the electroless plating technique, is the recognition that palladium pre-treatment in not necessary to assist the cobalt deposition reaction.

The experiment in which the support was pre-treated with nitric acid was undertaken to assess whether nitric acid modified the absorption characteristic of the alumina support. The data, when compared with data in Table 3.1, indicate that a drastic effect on the Vp/Vc ratio is obtained after the acid treatment.

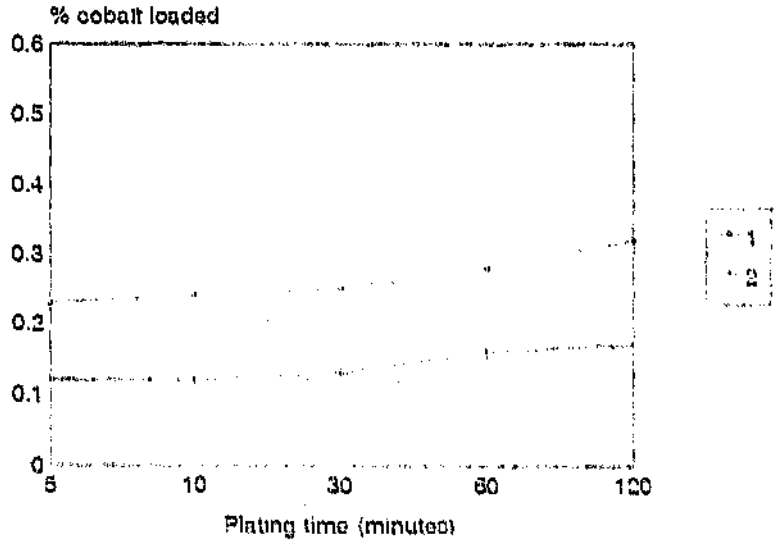


Figure 3.16. The effect of surface activation treatment on the impregnation of cobalt (%).

1) No surface activation.

2) Surface activation with palladium nitrate (pH 2,00).

3.2 DISCUSSION: ELECTROLESS PLATING OF COBALT ON ALUMINA

3.2.1 Impregnation of cobalt from a cobalt nitrate solution with and without surface activation.

A comparison of the data obtained in sections 3.1.1 and 3.1.2 are shown in figure 3.16. Surface activation treatment in section 3.1.2 consisted of 1 g/l palladium nitrate at pH 2,00.

It can be clearly seen that, in the absence of a surface activation treatment, that a near equilibrium amount of cobalt loaded is rapidly established and thereafter only a very small amount of extra cobalt is added to the support as a function of time.

In the presence of a surface activation treatment, it is to be noted that i) the pre-treatment with palladium resulted in a decrease in cobalt uptake, and ii) a near equilibrium uptake of cobalt was rapidly achieved followed by a slow increase in cobalt uptake with time.

It can be seen from the data shown in figure 3.16 that the percentage metal loaded onto the support pellets in the case of no surface activation treatment was almost twice as high as in the case where the support pellets did undergo surface activation treatment. This suggests blockage of cobalt uptake in the presence of palladium surface activation. The uptake of cobalt was however low in both cases Due to the low metal loadings obtained, the penetration profile could not be measured by optical microscopy, and no comment can be made on the Vp/Vc ratios for this data.

After a long and protracted investigation it became apparent that the phenomenon being observed did not appear to be electroless plating. In early experiments, both the enhanced loadings using the bath mixtures, when compared to the simple addition of cobalt to alumina, as well as the grey cobalt oxide appearance of the new catalyst were suggestive of electroless plating (see Chapter 3). However it was eventually noted that neither a reducing agent nor a palladium pre-treatment process were needed to obtain high cobalt loadings on alumina.

What has been noted is the importance of citrate ions to achieve these results and the role of pH of the pre-treatment in influencing the Vp/Vc ratios.

Thus the experiments have indeed revealed how numerous variables associated with physical properties (e.g. temperature) and chemical reagents can control loadings and Vp/Vc ratios. In this sense the project has been a success.

However the thesis results have now opened up a range of new directions for the synthesis of supported catalysts.

1) From the literature it is clear that electroless plating can be used to synthesize catalysts. Work published since our initial investigations have shown that copper can be plated on inert supports. Our own work in this area on copper confirms this. Thus a more careful consideration of the support pre-treatment experiments need to be carried out. This will initially involve the use of $SnCl_4$ to act as an initiator. In later studies the removal of the $SnCl_4$ and replacement by other non-chloride ion initiators will need to be determined.

CHAPTER 5

CONCLUSION

The results obtained in this study were totally unexpected. As a consequence some re-thinking of the strategy on the use of the electroless plating procedure to synthesize catalysts is required.

In the original motivation for the use of the electroless plating technique, it was proposed as a procedure for the synthesis of catalysts with high metal loadings and variable Vp/Vc ratios. Numerous "baths" to synthesize catalysts on inert supports have been reported in the literature, but the procedures appeared inappropriate for the synthesis of catalysts. This arose ince most baths included the use of Cl^- ions in their composition. Further, since inert supports required "roughening" to ensure the metal would stick to the support, use of supports such as Al_2O_3 would alleviate this process. Indeed preliminary studies by Colley confirmed this proposal.

A range of experiments were thus carried out to assess the role of the variables in obtaining catalysts with different cobalt loadings and Vp/Vc ratios. Gold baths were similarly optimized.

Table 4.2 Gold loadings and penetration profiles of Au/Al_2O_3 catalysts evaluated for the hydrochlornation of acetylene.

% GOLD PRESENT	Vp/Vc RATIO	CONVERSION BEFORE REDUCTION	CONVERSION AFTER REDUCTION
0,23	0,23	0	0
0,53	0,11	0	0
0,97	0,17	0	0
1,04	0,18	0	0
1,10	0,42	0	0
1,32	0,12	0	0
1,83	0,17	0	0
1,87	0,23	0	0
2,42	0,23	0	0
2,70	0,23	0	0

Remarkably none of the catalysts showed any activity. This is a surprising result. In previous work Au/C catalysts showed high activity for the reaction. Preliminary data obtained by Nkosi revealed that Au/Al_2O_3 gave poor activity, but activity which increased with gold loading. Typical gold loadings used were 0,5 - 1%.

In order to confirm that the reactor and gas chromatograph combination used functioned correctly, some Au/C catalysts were prepared under conditions established to produce relative high gold loadings. These Au/C catalysts were subjected to the same procedure as the Au/Al_2O_3 catalysts, and high activities were obtained. These were only used as control samples, and the exact conversions obtained were not noted. It was however established that the reactor assembly performed satisfactory.

At this stage no explanation can be given for the lack of catalytic activity of the new catalysts.

Clearly the Vp/Vc ratio then plays an effect in Co/Al_2O_3 catalysed POX reactions. It must be emphasized that the effect of Vp/Vc ratio must not be related directly to a diffusional argument. Since the catalyst has been ground up, the portions of support with and without catalyst have been intensively mixed together, on average it can be expected that the catalyst with Vp/Vc ratio of ~ 1 will have a more average cobalt loading throughout the pressed and sieved powder. The explanation for this effect will have to be sought in later experiments.

The influence of possible "impurity ions" which arise from the unusual synthesis procedure used will have to be carefully considered in evaluating the results. What is clear however is that the way in which the catalyst is synthesized has a dramatic effect on the catalytic activity.

4.2 Hydrochlorination of acetylene over alumina-supported gold catalysts.

The catalysed hydrochlorination of acetylene provided a test for the catalytic activity of the gold catalysts prepared in this work. In previous studies (30) procedures for evaluating gold catalysts were developed.

A series of gold catalysts for testing were prepared as described in the experimental section. A range of the catalysts with varying gold concentrations and Vp/Vc ratios were prepared. The results obtained are shown in table 4.2.

Table 4.1 Conversions obtained with various Co/Al_2O_3 catalysts.

% COBALT PRESENT	Vp/Vc RATIO	% CH_4	% CONVERSION
0,73	0,22	62,6	37,4
0,81	0,19	59,2	40,8
0,90	0,19	50,5	49,5
1,01	0,23	36,1	63,9
1,74	0,97	68,5	31,5
2,50	0,96	72,0	28,0

Two trends are apparent from the data obtained:

1) If the % cobalt loading is increased (0,64 to 1,01%) at a near constant Vp/Vc ratio then the % conversion increases (37,4 to 63,9%). Interestingly at higher loadings (1,47 and 2,50%) and a different constant Vp/Vc ratio the % conversion is near constant (slight drop from 31,5 to 28,0%). It is thus apparent that no advantage is to be seen using cobalt loadings exceeding 1%. This has been noted previously for conventionally prepared Co/Al_2O_3 catalysts (14).

2) Increasing the Vp/Vc ratio (0,22 to 0,96) decreased the conversion rate. It is to be noted that the % cobalt loading has been varied in these experiments, but other data on conventionally prepared Co/Al_2O_3 catalysts have indicated constant activity with loadings above 1% cobalt (14).

CHAPTER 4

AN EVALUATION OF THE NEW SUPPORTED COBALT AND GOLD CATALYSTS.

4.1 Partial oxidation of methane over alumina-supported cobalt catalysts.

The partial oxidation (POX) of methane is a reaction of great industrial importance. In our laboratories, Co/Al_2O_3 have been intensively tested for the reaction. The POX reaction thus provides a very simple probe reaction for the evaluation of the new Co/Al_2O_3 catalysts. In this way the effect of both loading and Vp/Vc ratios on the POX reaction can be tested. It is to be noted that the Vp/Vc ratios relates to the pellets used in the loading procedure. However, the pellets were ground up after cobalt loading, pressed, then reground and sieved.

A series of catalysts with different cobalt loadings and Vp/Vc ratios where then tested for the POX reaction:

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2$$

The catalysts tested were obtained during the evaluation of the effect of the pH of the plating bath on the impregnation of cobalt and the penetration of cobalt [section 3.1.7(a)], as well as during the evaluation of the effect of exposure time on the above (section 3.15).

The reaction conditions used were described in the experimental section and conform to conditions used in other studies (J.C. Jeannot, M.Sc. Thesis). Data obtained in the experiments are shown in Table 4.1.

From table 3.18, it was shown that the % metal loaded maximized at a temperature of 60 °C and decreased towards 80 °C. Cobalt plating showed a continuous increase in % metal loaded up to 80 °C.

When the optimum support plating time was determined, as shown in table 3.19, it was found that the % gold loaded was again a function of plating time. Relatively high metal loadings in the case of gold were obtained, when compared with cobalt.

When the effect of different potassium hydroxide concentrations on the metal loading and the penetration profile was determined as shown in table 3.20, it was found that an optimum gold loading was obtained at a potassium hydroxide concentration of 35 g/l.

It was shown in sections 3.3.1 to 3.3.4 that a gold loading of up to 4,68% can be obtained by varying the parameters studied, and that optimum conditions exist for selecting desired metal loadings and penetration profiles when preparing gold catalysts supported on alumina.

Finally it must be stressed that while the ability to control Vp/Vc ratios and gold loadings have been established, it has not conclusively been shown that the phenomenon relates to electroless plating. This was the assumption made in devising the project. Clearly the work on cobalt has shown that the mechanism does not appear to relate to a redox process. More work, outside the scope of this thesis, will be needed to further probe the concept of electroless plating of gold for catalytic purposes.

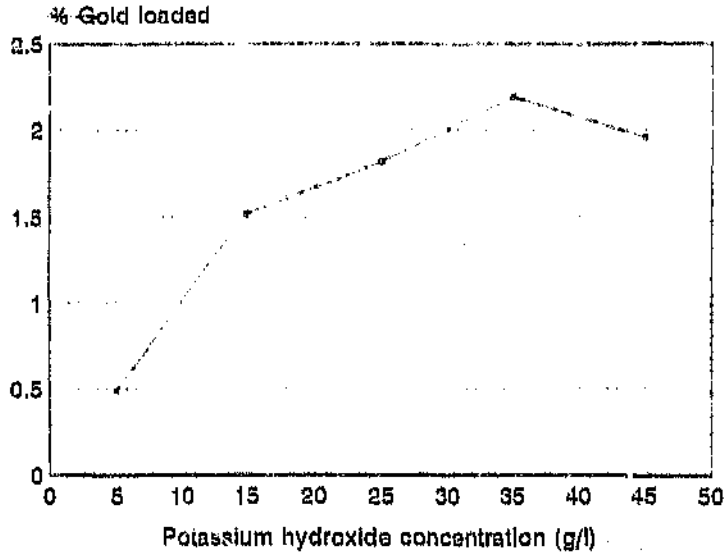


Figure 3.22(a). The effect of variation in potassium hydroxide concentration of the plating bath on the impregnation of gold (%).

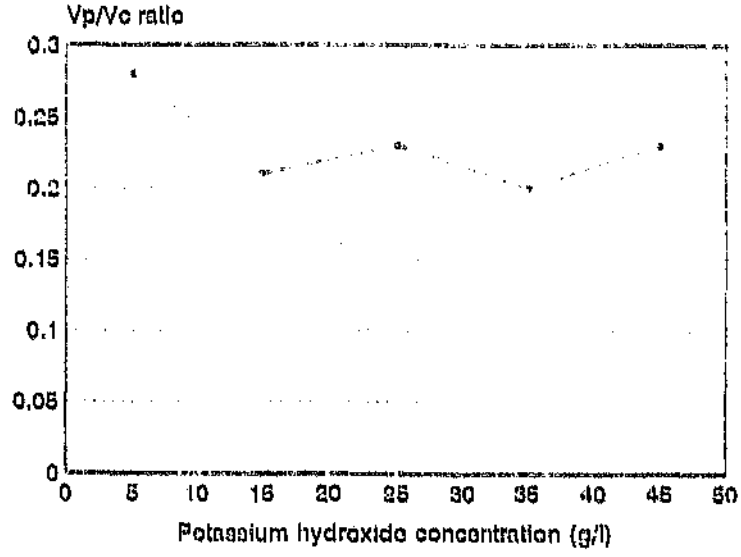


Figure 3.22(b). The effect of variation in potassium hydroxide concentration of the plating bath on the penetration profile.

Table 3.20 The effect of variation in potassium hydroxide concentration of the plating bath on the impregnation of gold and the penetration profile.

POTASSIUM HYDROXIDE, g/l	Vp/Vc RATIO	GOLD LOADED, %
5 g/l	0,28	0,49
15 g/l	0,21	1,52
25 g/l	0,23	1,82
35 g/l	0,20	2,19
45 g/l	0,23	1,96

It is shown in table 3.20. that the penetration profile is independent of variation in potassium hydroxide concentration. The % gold loaded onto the support showed a maximum at a potassium hydroxide concentration of 35 g/l.

3.4 DISCUSSION: ELECTROLESS PLATING OF GOLD ON ALUMINA.

Completely different plating bath formulations were used for the electroless plating of cobalt and gold. However, comparisons are still possible between the two systems and these are discussed below.

It is shown in table 3.17 that the penetration profile of the gold into the support as well as the % metal loaded was determined by the pH of the activation solution. Both penetration and mass of metal loaded is therefore a function of the pH of the activation treatment. The cobalt plating results showed however that only penetration profile, and not the % metal loaded, was a function of pH of the activation treatment.

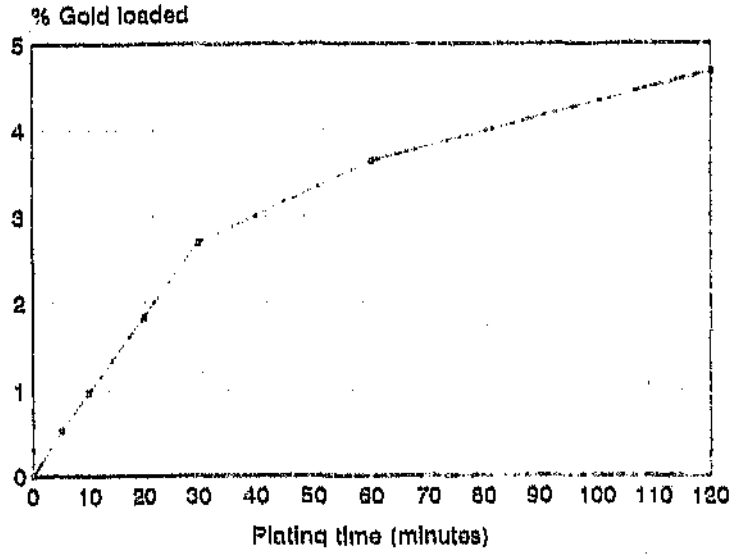


Figure 3.21(a). The effect of variation in support exposure time on the impregnation of gold (%).

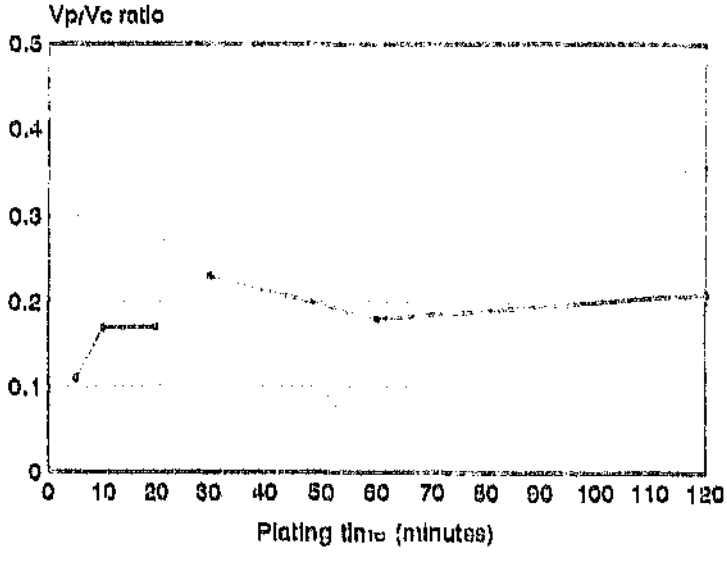


Figure 3.21(b). The effect of variation in support exposure time on the penetration profile.

Table 3.19 The effect of variation in support exposure time on the impregnation of gold and the penetration profile.

EXPOSURE TIME, minutes	Vp/Vc RATIO	GOLD LOADED, %
5	0,11	0,53
10	0,17	0,97
20	0,17	1,83
30	0,23	2,70
60	0,18	3,65
120	0,21	4,68

3.3.4 Determination of the effect of variation in potassium hydroxide concentration of the plating bath on the impregnation of gold and the penetration profile.

The plating bath formulation described in table 2.4. was used, but the potassium hydroxide concentration was varied between 5 g/l and 45 g/l. The procedure described in section 2.4.3. was followed. The temperature of the plating bath was maintained at 60 °C, and the pH of the activation solution at 2,00. Exposure time was kept constant at 30 minutes. The data obtained are listed in table 3.20. and shown in figures 3.22(a) and (b).

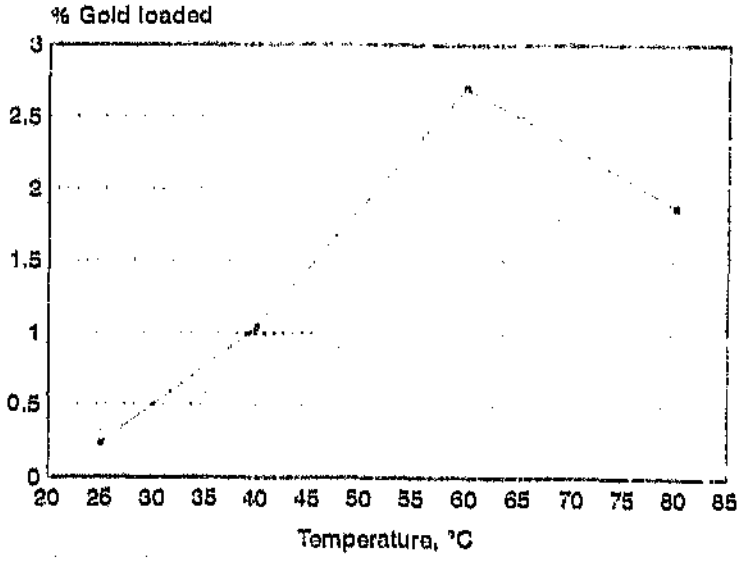


Figure 3.20(a). The effect of variation in temperature of the plating bath on the impregnation of gold (%).

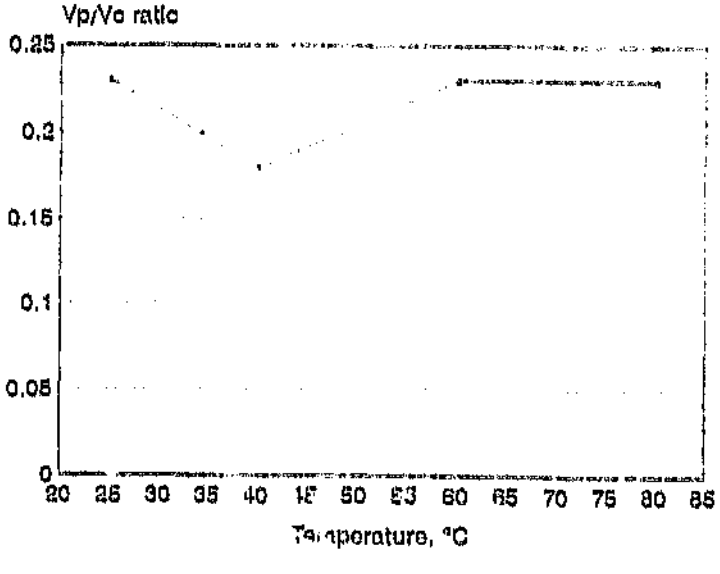


Figure 3.20(b). The effect of variation in temperature of the plating bath on the penetration profile.

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APPENDIX 1

1. Publication arising from this thesis.

Coville, N.J., Colley, S.E., Beetge, J.A. and Orchard, S.W. *"Proceedings of the 10th International Congress on Catalysis, 19-24 July, 1992, Budapest, Hungary - The Synthesis of Cobalt Supported Catalysts by Electroless Plating Techniques - Elsevier Science Publishers"* 1993, 1743 - 1746.

2. Conference presentation arising from this thesis.

Poster Presentation - Catalysis Conference 1991 - Highlands National Park, Golden Gate.
The Synthesis of Catalysts via Electroless Plating.
Data were presented on the synthesis of supported cobalt on Al_2O_3 via the technique of electroless plating.

2) If citrate ions play such an important role in the loading, then clearly a study of citrate analogues is necessary. Is there anything special about the citrate ion? There are reports in the literature of the use of citrate ions in loading studies (31) and this effect needs more substantial investigation. Also of note is the known ability of the citrate ion itself to act as a reducing agent (32).

3) Clearly Vp, Vc ratios can now be varied with the approach described in this thesis. The ability to vary Vp/Vc ratios in the Fischer-Tropsch reaction have recently been described by Iglesia and co-workers (33) for some cobalt catalysts, and this paper provides an important overview on recent work on catalyst support studies. More testing reactions need to be performed to assess the relationship between loading, Vp/Vc ratio and catalyst activity. In this thesis the objective was to do preliminary testing work, and the data on both the cobalt and gold catalysts have revealed poor activity for the new catalysts. Much time was spent in performing the experiments listed (and many others not listed). However many more studies will have to be performed to confirm the data observed here.

Author: Beetge Johannes Albertus.
Name of thesis: Electroless plating- a technique for the preparation of supported cobalt and gold catalysts.

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