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CHAPTER 2
EXPERIMENTAL

2.1 Materials

The following reagents or samples were used during the study to recover high value metals from the spent catalyst:

- A sample of the waxy lumps of the spent catalyst produced by Sasol was used as the feedstock of high value metals like Co, Pt and Al.
- A commercial sodium hydroxide solution (25 – 50 % NaOH) produced by Sasol Polymers (formerly Polifin Limited) at Sasolburg was used to selectively dissolve alumina from the spent catalyst.
- Chemically pure mineral acids such as sulphuric acid (98 % H_2SO_4) and hydrochloric acid (32 % HCl) were supplied by Merck NT and Promark Chemicals Industries, respectively. These acids were used as lixiviants during the leaching step. Commercial nitric acid (56 % HNO_3) was manufactured by Sasol Mining Explosives (SMX), a division of Sasol Chemical Industries and was used as a leaching agent during the dissolution of cobalt species from the cobalt containing residue. This acid was also used to strip cobalt species loaded into the organic phase during the solvent extraction step.
- Chemically pure ammonium hydroxide solution (10 - 25 % NH_4OH) was supplied by Merck NT and was used to precipitate both Al and Fe from the leach liquor solution prior to the application of the solvent extraction step.
- Di-2-ethylhexyl phosphoric acid (D2EHPA) and tributylphosphate (TBP) were obtained from Rustenburg Refiners (Base Metal Plant). Natref at Sasolburg produced the illuminating paraffin used. These organic materials were mixed to produce an organic phase which was used to extract cobalt species from the leach liquor solution during the solvent extraction step.
- Commercial cobalt nitrate and tetraammine platinum nitrate were obtained from other vendors and they were used as the cobalt and platinum precursors respectively during the manufacture of the original catalyst.

- A commercial alumina labelled as Puralox SCCa2/150 was produced by Sasol Chemie (formerly Condea Chemie GmbH (Hamburg Germany)). It was used as a support during catalyst preparation,
- Kynochem, a member of the AECI group of companies, supplied a commercial aluminium hydroxide. The latter was used as a standard during the comparative study of the aluminium hydroxide originating from the Sasol proprietary spent catalyst,
- Zetachem Company produced a cationic flocculant labelled ZN92V Zetafloc. It was used to flocculate the suspended particles from the leach liquor solution produced during the dissolution of cobalt species from the leached spent catalyst residue.
- Modified polyacrylamide flocculants labelled as Superfloc®HX200, HX300 and HX400 were produced by Cytec. These flocculants were utilised during the flocculation of the slurry produced during the leaching of the Sasol proprietary spent catalyst with sodium hydroxide solution.

2.2 Methods and instrumentation

The laboratory instruments as well as methods used in this study are briefly described as follows:

A Vista AX CCD simultaneous ICP-AES instrument was used to determine concentrations of elements present in the spent catalyst and its derivative products. The loss on ignition (L.O.I.) of samples to be analysed was initially determined at 600 °C prior to the ICP-AES measurements. Approximately 4 ml of concentrated sulphuric acid (98 % H_2SO_4) and 15 ml of hydrofluoric acid (70 % HF) were added to 0,4 g of either spent catalyst, catalyst, catalyst-derived ash or spent catalyst derived salts. This mixture was then evaporated to 1 ml in order to completely dissolve the solids. The solution was allowed to attain ambient temperature and subsequently transferred into a large beaker. Approximately 10 ml of hydrochloric acid (2,2 % HCl) was added to the cooled solution and the

latter solution was again evaporated to 10 ml to completely dissolve the remaining solids. After the digestion, the solution was diluted to 250 ml and acid insoluble residues were separated through filtration. Finally 10 ml of the final filtrate was transferred by pipette and diluted with water to 100 ml. Subsequently the concentration of the element present in the liquid sample was determined using the ICP- AES instrument. The concentration of the standard solution was also determined. Finally, the concentration of the element found present in the sample was reported as ppm, g/l or %.

The catalyst containing platinum was initially milled prior to the platinum determination until a particle size of 90 % < 75 µm was obtained. Approximately 0,1 g of the milled sample was weighed out on the analytical balance and subsequently placed in an appropriate dish. The sample was then roasted at 500 °C in a furnace for eight hours. Approximately 0,1 g of the roasted sample was mixed with 3 g of an appropriate flux. The flux used in this analysis was originally prepared with 60 g silica, 125 g sodium carbonate, 70 g lead oxide, 45 g borax, 4 g cobalt and 60 g lithium oxide. Thereafter the mixture was transferred to an appropriate pot. Eventually, it was mixed with 1 ml of 1M $AgNO_3$ solution and the mixture was fused in a furnace, preheated to 1100 °C for 1 h. The pot containing the slag formed during fusion step was allowed to reach ambient temperature and eventually the slag was recovered from the pot. The lead button was cupelled at 1000 °C for 1 h period. The cooled prill was transferred to a test tube and approximately 5 ml of aqua regia was added to the test tube. Afterwards, the mixture was heated in a microwave oven for 20 min to complete the dissolution of platinum. The solution was then diluted to a 5 ml volume and the platinum present in the solution determined by means of ICP spectrometry.

A method number 010-002_AICP-aqua-Regia 010-002 is briefly prescribed as follows:

Five standards with appropriate concentrations using the acid mixture, as diluents were prepared. The ICP spectrometer was allowed to warm up for 20 min and a *wavelength calibration was performed at the beginning of the session*. A wavelength resloping procedure was performed at every 50th sample of each *analytical run. The ICP spectrometer was set on the optimum excitation* and analytical conditions as previously determined. A calibration for every element to *be determined using the prepared standards* was performed and the calibration curve of each element was checked. Finally the samples were analysed and their *concentrations of the elements present in the sample* were *reported as ppm, g/l or* %.

An XRF spectrometer (courtesy of Phillips Electric Instruments) was used to *investigate the characteristic spectra* of elements present in a solid sample. For quantification analysis, the intensity of characteristic lines of the element to be *analysed was measured. Elements such as* Al, Fe, Si, Co, S and trace element like Pt are contained in the spent catalyst and it's derivative metal salts. These solid *samples were analysed for above elements by* XRF as follows:

A coarse solid sample (spent catalyst and its derivative products) was initially ground until a particle size of 100 % < 200 µm was obtained. The powdered sample was now *calcined at 850 °C for 4 h in order to* remove all organic compounds and water originally contained in the sample. The calcined sample was then converted *into a solid solution by fusion with* lithium tetraborate ($Li_2B_4O_7$).

The prepared solid solution and standard (NFMN from Mintek) were placed in the sample holders. The *sample holder was then placed* in the sample compartment of an XRF spectrometer. The intensity of a characteristic line of the element to be determined was measured *and the concentration* of the element in the sample was calculated from the intensity measured (Matjie, 1997).

An H18521 Hanna pH meter with both glass electrode and temperature probe (automatic control) was utilised in the laboratory to measure the pH and temperature of an aqueous solution during the leaching and precipitation steps of the proposed process of recovering high value metals from the spent catalyst.

XRD analysis was performed on a Siemens diffractometer employing Ni-filtered Co Kα radiation (1.7902 Å). The ASTM powder diffraction file was used to identify the phases present. The conditions at which the diffractometer was set for the qualitative identification of the phases in the support are stated in Table 2.1.

Table 2.1: Experimental conditions for XRD analysis

Parameter	Setting
Voltage	40 kV
Current	25 mA
Divergence slit	1°
Receiver slit	0.15°
Scanned from	X*2θ
Scanned to	Y*2θ
Counting time	2s

*X and Y define the 2θ scanned range.

Coarse samples (spent catalyst, spent catalyst derived metal salts) to be analysed were initially ground using a ball mill in order to obtain < 200 μm sized particles. The powdered sample was transferred to a suitable sample holder (preferably made of aluminium) and the sample in the holder was tamped gently, but thoroughly, with the edge of a glass slide. It was important to fill the sample holder and thereafter the surplus sample was "sliced" off with a glass slide (approximately 50 X 70 mm and 5 mm thick) whilst simultaneously compressing the sample in the holder. The above procedure was repeated until a suitable surface (a smooth surface of even texture) was obtained.

After preparation of the sample surface, the sample holder was placed in the sample compartment and scanning of the sample commenced (Matjie, 1997, Coffey, 1976 and Klug and Alexander, 1954).

A Tri-Star 3000 Micromeritics instrument was employed to measure the BET surface area and pore volume of catalysts prepared with cobalt nitrate originating from the spent catalyst. The BET surface area and pore volume measurements of the alumina emanating from the spent catalyst were also performed on the same instrument. In this analysis, approximately 0.25 g of the analyte was accurately weighed into the sample tube and degassed in the degas unit at 200 °C using a constant nitrogen flow. The contaminants adsorbed in the sample were probably removed during this degassing step. The degassed sample was reweighed in order to determine the mass of the catalyst. Finally the dead volume glass tube was inserted in the instrument and the surface area of the sample as well as its pore volume was measured. The surface area and pore volume of the analyte obtained in this experiment are reported in m^2/g and cm^3/g respectively.

A Micromeritics TPD/TPR 2900 instrument was used to determine the amount of reducible species present at different temperatures. Approximately 0.15 g of the analyte was accurately weighed out and placed on a porous plate mounted in a ¼ inch U- shaped quartz tube. Subsequently, this tube was connected to the analysis ports and argon gas was flowed through with an in-line a Dewar flask with cold trap surrounded by coolant. The trap served to collect the condensable products before the gas was directed through the thermal conductivity detector. The argon gas flow was subsequently terminated and the analyte then exposed to 10 % H_2-Ar gas mixture as a reducing gas flowing at a rate of 50 Ncm^3 min^{-1}. The furnace was ramped from room temperature to 800 °C at a rate of 10 °C min^{-1}. After the completion of the experiment the sample tube was cooled down under stream of argon (50 cm^3 min^{-1}).

A Leo 1430 Scanning Electron Microscope (SEM) operating at 3 kV was employed to produce images of the particles of the catalyst surface in order to determine their morphology. In this analysis, the sample was adhered to double sided carbon-tape stuck onto an aluminium stab and followed by gold sputtering for 30 s (a total of four times) to render the particles conductive.

A Saturn DigiSizer 5200 v1.03, Micromeritics instrument was employed to determine the particle size of the catalyst prepared by cobalt nitrate originating from the spent catalyst. A pump with the speed of 35 rpm was used in the experiment in order to suck the sample particles (Maripane, 2001).

2.2.1 Calcination of the spent catalyst

Waxy lumps (approx. 1000 g) of the spent catalyst were placed in a stainless steel dish. A gas burner was used to ignite the waxy lumps in the presence of air. A self–supporting combustion of the spent catalyst under natural convection was carried out for two hours until no further combustion took place. In order to oxidise All carbonaceous materials remaining in the calcined spent catalyst, a free flowing sample produced during this process was recalcined at different temperatures ranging from 600 - 1000 °C for six hours in the presence of air. A sample produced in this experiment was prepared and submitted for phase identification using XRD and was subjected to also carbon analysis. A second representative free flowing sample was mixed with sodium carbonate using solid to solid ratio of 1:1 (m/m) and the mixture was finally recalcined under the above conditions. Subsequently, a free flowing sample produced after a self-supporting combustion step as well as samples produced after calcining the spent catalyst at various temperatures were submitted for carbon analysis.

2.2.2 Leaching of the calcined spent catalyst with sodium hydroxide

Approximately 420 g of the calcined spent catalyst (calcined with or without sodium carbonate) was added to a 2500 ml Teflon vessel containing about 1260 g of either 25 % w/w NaOH or 50 % w/w NaOH. The resultant slurry was heated to

170 °C in a high-pressure autoclave for 4 h, with pressure of the slurry being increased from 0 - 12 bar. After cooling the autoclave, the slurry sample was collected and washed with 1000 ml of water to remove the residual slurry from the vessel. The resultant slurry sample was reserved for the flocculation testwork described in Section 2.2.7.

A schematic presentation of the high temperature autoclave is given in Figure 2.1.

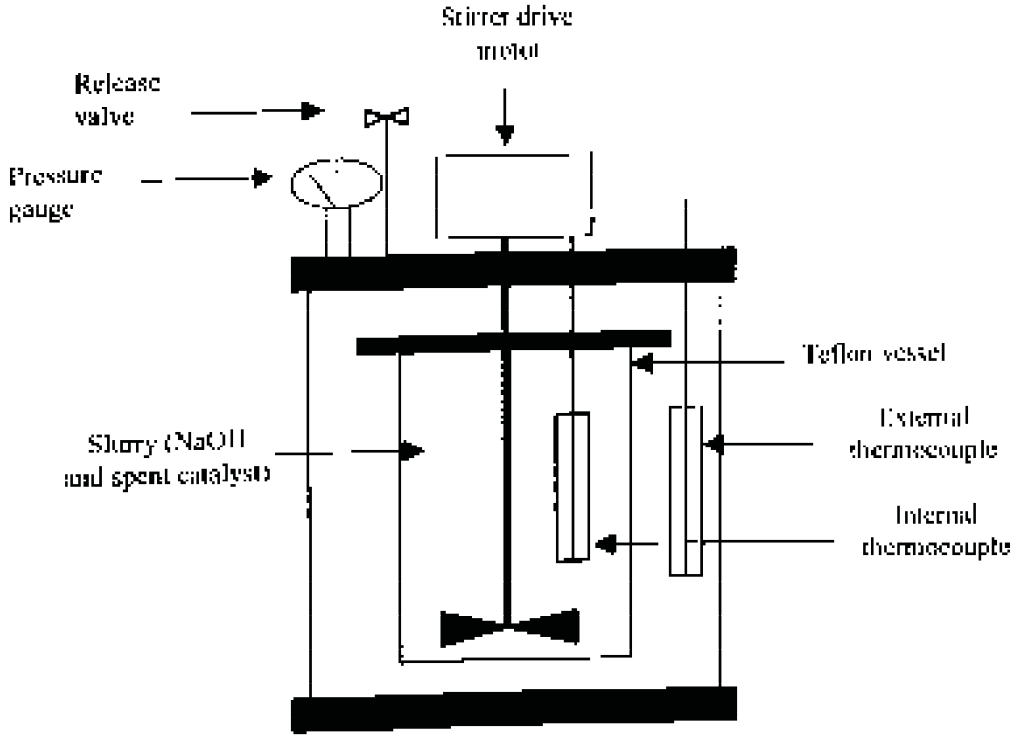

Figure 2.1: Schematic presentation of the high temperature autoclave for leaching the spent catalyst.

To further improve the aluminium extraction efficiency, two further leaching steps were used to solubilise the remaining aluminium species from the calcined spent catalyst. The filter cake obtained from the first leaching step was contacted with fresh sodium hydroxide solution (using either 25 % w/w NaOH or 50 % w/w NaOH) and finally the slurry was further leached under the above-mentioned conditions. Following the leaching step, the residue was separated from the solution through filtration using filter press. Subsequently, 1000 ml of water was

used to remove the residual leach liquor solution absorbed in the filter cake. The water-washed residue was dried at 90 °C. Subsequently the dried washed residue as well as the leach liquor solution was prepared and submitted for Co, Pt and Al analysis. In a separate experiment, sodium hydroxide solution (about 64 g of 20 % w/w NaOH) was allowed to react with calcined spent catalyst (about 25 g) at 90 °C at atmospheric pressure. After filtration, washing and drying, the sodium hydroxide insoluble residue was submitted for Co, Pt and Al analysis.

In order to confirm the preliminary results obtained after leaching the spent catalyst with sodium hydroxide solution, 30 kg of the calcined spent catalyst was placed in a 400 l high-pressure autoclave. Approximately 120 l of 25 % NaOH was added to the auto-clave and leaching performed at various temperatures and pressures for 4 h. Approximately 100 ml of the slurry was collected from the autoclave at hourly intervals and was subsequently flocculated prior to filtration. The procedure followed during the flocculation step outlined in Section 2.2.7. Following the filtration step, the sodium hydroxide insoluble residue was produced and thoroughly washed with 100 ml of distilled water in order to remove residual leach liquor solution. The washed residue produced in this way, was dried at 90 °C and the resulting residue as well as the filtrate were submitted for analysis (Matjie, 2000).

2.2.2.1 Effect of temperature, time and pressure on metal solubilisation during sodium hydroxide leaching

Testwork was conducted on the calcined spent catalyst in order to determine the effect of temperature, pressure and leaching time on aluminium, cobalt and platinum solubilisation using sodium hydroxide solution (25 % NaOH) at a solid to liquid ratio of 1:4 (m/m). The experiment was performed in an autoclave at various temperatures (in the range 27 - 190 °C) and pressures (in the range 0 - 12 bar). During the leaching step, a slurry sample was taken from the autoclave at hourly intervals. Each sample thereby obtained was initially flocculated prior to filtration.

The experimental method described earlier in Section 2.2.2 for preparing samples for analysis was applied.

2.2.2.2 Effect of leaching time on metal solubilisation

The leaching temperature (approximately 190 °C) of the slurry was fixed during the leaching step and a slurry sample was then taken out at hourly intervals and submitted for both ICP analysis and XRF analysis (using the fusion method). The concentration of each element present in the sample was reported as % or g/l.

2.2.3 Leaching of the calcined spent catalyst with hydrochloric acid solution

To test whether cobalt could be selectively dissolved from the spent catalyst with i.e. no substantial dissolution of aluminium, the calcined spent cobalt catalyst was leached with hydrochloric acid solution (about 15 % HCl) at 90 °C for various times in the range 2 – 5 h. The experiments were conducted at different solid to liquid ratios (in the range 1:1 - 1:4 w/w). Two leaching steps were also used to further improve cobalt extraction efficiency. The leached residue was separated from the leach liquor solution by normal filtration. Subsequently, the residue was thoroughly washed with water in order to remove the leach liquor solution retained during filtration. Subsequently, the dried washed residue as well as the leach liquor solution was submitted for ICP analysis. Finally, the extraction efficiency of metal ions present in the leach liquor solution was calculated and reported on a percentage basis.

2.2.4 Leaching of the calcined spent catalyst with nitric acid solution

Approximately 322.5 g of 20 % of HNO_3 was placed into a 1000 ml beaker. About 25 g of the calcined spent catalyst was then added and eventually heated to 90 °C at atmospheric pressure for 3 h. Subsequent to the leaching step, the residue was separated from the leach liquor solution by normal filtration and thoroughly washed with sufficient water in order to remove the residual leach liquor solution from the filter cake. After drying the washed residue at 90 °C to remove free water,

the residue was ground to the desired particles size and submitted for Co, Al and Pt analysis. The extraction efficiency of the metals present in the leach liquor solution was calculated and was reported on a percentage basis.

2.2.5 Leaching of the calcined spent catalyst with sulphuric acid solution

Approximately 260 g of 20 % of H_2SO_4 was placed into a 1000 ml beaker and together with 25 g of the calcined spent catalyst. The mixture obtained in this way, was heated to 90 °C at atmospheric pressure for 3 h. After the leaching step, the sulphuric acid insoluble residue was successfully separated from the leach liquor solution and washed thoroughly with water in order to remove the residual leach liquor solution by normal filtration. After drying this residue at 90 °C for 3 h to remove free water, the dried residue was submitted for Co, Pt and Al analysis. Eventually the extraction efficiency of the metals present in the leach liquor solution were calculated and reported on a percentage basis.

2.2.6 Leaching of the calcined spent catalyst with water

Approximately 420 g of the calcined spent catalyst (calcined with sodium carbonate) was added to a 5000 ml beaker containing about 1260 g of water. This slurry was heated to 90 °C at atmospheric pressure for 4 h. After the leaching step, the water-insoluble residue was separated from the leach liquor solution by normal filtration and washed thoroughly with sufficient water to remove the residual leach liquor solution from the filter cake. After drying this residue at 90 °C for 3 h to remove free water, the dried residue was submitted to SCI laboratories for Co and Al analysis. Eventually the extraction efficiency of the metals present in the leach liquor solution were calculated and reported on a percentage basis.

2.2.7 Flocculation on the slurry from the alkaline and acid leaching steps

After leaching the calcined spent cobalt-based catalyst with sodium hydroxide solution (about 25 % w/w NaOH) at high temperature (200 °C) and pressure (15

bar), the resulting slurry typically contains ultra fine solid particles dispersed in sodium aluminate-containing solution. This slurry was filtered only with difficulty and might possibly render the proposed process of recovering high value metals impractical. The procedure described below was used in all experiments conducted on the slurry in order to flocculate the suspended material.

Approximately 2 % w/w of polyacrylamide flocculant was prepared using sodium hydroxide solution (about 2 % w/w NaOH). The solution was then conditioned at ambient temperature for 1 h in order to form a homogeneous solution. It was further diluted with sodium hydroxide solution (2 % w/w NaOH) to produce a final solution containing about 0.25 % w/w of the flocculant.

Approximately 3000 - 6000 g/t of the modified polyacrylamide (0,25 % flocculant) heated to 90 °C was added to the boiling slurry and mixed thoroughly until the flocs were formed. These flocs were separated from the mixture by filtration and eventually washed with water to remove the aluminium-containing filtrate absorbed during filtration. The turbidity of the filtrate was measured prior to aluminium analysis. The filtrates as well as the dried flocs produced in this way were submitted for aluminium analysis.

Alternatively, approximately 2000 g of the acidic leach liquor solution from the leaching step was mixed with 500 ml of 0,1 % ZN92V Zetafloc. The slurry was heated to 60 °C with stirring and subsequently conditioned for 10 min. Sticky flocs were formed and were found to settle rapidly. The leach liquor solution was separated from the flocs by decantation. The flocs were washed with 500 ml of water at 60 °C to remove the residual leach liquor solution absorbed during the flocculation step and finally the flocs were dried at 90 °C and reserved for subsequent treatment. The leach liquor solution together with the dried flocs was submitted for ICP analysis.

2.2.8 Selective dissolution of cobalt from the basic leached residue by nitric acid solution

Approximately 128 g of the leached residue was dissolved in a nitric acid solution (about 400 g of 55 % w/v of nitric acid) at 100 °C for 4 h. The experiment was conducted at atmospheric pressure. The slurry formed from this leaching step was filtered at room temperature to obtain a filter cake. The washing step was included in the experiment using a filter cake to water ratio of 1:4 (m/m) to remove the residual leach liquor retained after the leaching step. The wash solution was then combined with the leach liquor solution to form the final parent solution. After drying the washed filter cake, the twice-leached residue was weighed out prior to undertaking the cobalt, platinum and aluminium analysis. The impure cobalt containing solution was also submitted for analysis of these three elements.

2.2.9 Platinum dissolution

The residue produced during the nitric acid leaching was first calcined at 700 °C for 6 h in order to oxidise the flocculant present in the residue. Subsequently, 20 g of the nitric acid insoluble residue containing 7.67 % Pt was dissolved in 1000 ml of aqua regia (3HCl: 1HNO_3) at 80 - 90 °C at atmospheric pressure for 4 h to form chloroplatinic acid, H_2PtCl_6. Which was then separated from the aqua regia insoluble residue by filtration. The platinum acid obtained in this fashion could be reserved for the preparation of platinum sponge and various salts. The blue insoluble residue formed during the dissolution of platinum was dried at 90 °C prior to its submission for XRD analysis.

2.2.10 Crystallisation of platinum from chloroplatinic acid, H_2PtCl_6

Initially, chloroplatinic acid solution (1000 ml) was heated to 90 °C in order to remove unreacted nitric acid. Upon cooling the concentrated chloroplatinic acid solution, solid crystals were formed. Approximately 100 ml of hydrochloric acid was further added to the crystals and the mixture was evaporated to remove any remaining nitric acid from the crystals. Ammonium chloride solution (about 25 %)

was used to quantitatively precipitate the Pt(IV) from the platinic acid at 50 - 70 °C in the form of diammoniumhexachloroplatinate, $(NH_4)_2PtCl_6$. The deep-yellow crystals were isolated from the solution by filtration, dried at 50 °C and submitted for XRD and XRF analyses. The percentage yield of platinum from the spent catalyst was then calculated and reported on a percentage basis.

2.2.11 Calcination of diammoniumhexachloroplatinate

Approximately 0.2 g of diammoniumhexachloroplatinate contained in a silica crucible was calcined at 800 °C in the presence of air for 1 h. The calcined sample was submitted for XRD analysis.

2.2.12 Precipitation of iron and aluminium from the acidic leach liquor solution

Approximately 200 g of the impure cobalt-containing solution containing 5.2 g/l Al, 65 mg/l Pt and 68.3 g/l Co was transferred into a 1000 ml beaker. A solution of ammonium hydroxide (about 25 % m/v NH_4OH) was slowly added to the impure cobalt-containing solution and heated to 90 °C. Upon addition of ammonium hydroxide to the impure cobalt-containing solution, a gelatinous brown precipitate was formed at various pH values (in the range 4 - 5). The slurry was conditioned for 1 h and the precipitate was then separated from the solution by normal filtration (using a vacuum pump). Subsequently the precipitate was washed with sufficient water (200 ml) in order to remove the residual filtrate. The wash solution and the filtrate were combined at room temperature to form the final filtrate. This filtrate containing cobalt nitrate and ammonium nitrate was reserved for the solvent extraction step. A portion of the filtrate was then prepared and eventually submitted for cobalt, aluminium and iron analysis. The precipitate containing Fe and Al species could possibly undergo reaction with sodium hydroxide (about 25 % m/v of NaOH) to form sodium aluminate, which is eventually recycled to the precipitation of aluminium hydroxide step. The sodium hydroxide

insoluble precipitate containing Fe, may possibly be disposed of or dissolved in either sulphuric acid solution or nitric acid solution.

2.2.13 Purification of the filtrate produced during the precipitation step through solvent extraction method

The organic phase salt, which is suitable for the extraction of the Co(II) ions, was prepared as follows:

Approximately 800 ml of ammonium hydroxide solution (about 12,5 % w/v NH_4OH) was contacted with the organic phase containing 40 % w/w D2-EHPA, 20 % w/w Tributylphosphate (TBP) and 40 % w/w illuminating paraffin (about 2000 g of the organic phase) at room temperature. This mixture was stirred for 15 min and the two phases were allowed to separate at room temperature. The organic phase salt produced in this way contains ammonium ions and was suitable for the extraction of Co(II) ions from the filtrate at a pH of 4.1. Approximately 1000 g of the filtrate containing 18 mg/l Al, 4 mg/l Fe, 35 g/l Co and 3 mg/l Pt was transferred to a 5000 ml beaker. The pH of the filtrate was initially measured to be 4.1 at 70 °C. Approximately 2000 g of the organic phase salt was contacted with 1000 g of the original aqueous filtrate at 70 °C and was subsequently stirred for 5 min. The two phases were allowed to cool to room temperature and subsequently separated. The aqueous phase recovered after the solvent extraction step was submitted for the determination of Al, Pt, Co and Fe ions using ICP.

The loaded organic phase (about 2000 g) produced in this experiment was stripped with a solution of nitric acid (1000 g of 10 % HNO_3). The mixture was stirred at 70 °C for 5 min and eventually allowed to attain a room temperature. The two phases were rapidly separated and the aqueous phase recovered after the stripping step was submitted for the determination of Al, Pt, Co and Fe ions using ICP instrumentation. This aqueous phase was reserved for the crystallisation step that will be described in Section 2. 2.14 (Iler, 1978)

2.2.14 Crystallisation of aluminium trihydrate from sodium aluminate solution

After leaching the calcined spent catalyst with sodium hydroxide solution (about 25 % w/w NaOH), a leach liquor solution containing mainly sodium aluminate was produced. This solution was stored in a 1 l container for a 1 month. After this period, visual observation indicated that white crystals had formed in the solution. After filtration, washing and drying of the crystals, the final solid sample was submitted for XRD, PSD and elemental analyses. Eventually, the filtrate containing mainly sodium hydroxide and small amounts of sodium aluminate can be recycled to the leaching step where it can be utilized as a lixiviant.

2.2.15 Crystallisation of the cobalt nitrate

Approximately 150 ml of either impure acid leach liquor solution or the purified leach liquor solution was transferred into a separate 500 ml beaker. These solution typically contained 68.3 g/l Co, 5,2 g/l Al, 65 mg/l Pt and 326 mg/l Fe, and 7,7 g/l Co, 18 mg/l Al, 3 mg/l Pt and 4 mg/l Fe respectively. The leach liquor solution was heated to 90 °C until its volume was reduced by 50 %. The concentrated leach liquor solution was then added to a 250 ml crystalliser and upon cooling, red-brown crystals were formed. The crystals were separated by normal filtration and dried at 55 °C. The dried crystals were subsequently submitted for XRD analysis and elemental analysis. Concentrations of the substances present in the crystals were reported on a percentage basis (% w/w).

2.2.16 Calcination of aluminium trihydrate to form alumina

In an attempt to produce aluminium oxide, which is suitable for use in the Fischer-Tropsch catalyst, aluminium trihydrate produced during the crystallisation step

was calcined at various temperatures (in the range 400 - 600 °C) in the presence of air. A white powder product was formed and subsequently, both this product and the alumina currently used in the Fischer-Tropsch catalyst as a support material were submitted for XRD analysis.

2.2.17 Preparation of catalysts

Approximately 43,7 g of cobalt nitrate originating from the spent catalyst was dissolved in 40 ml of distilled water and 0,024 g of $(NH_3)_4Pt(NO_3)_2$ was also dissolved in 10 ml distilled water. Thereafter, the two solutions were mixed in a 500 ml round bottomed flask. Approximately 50 g of aluminium oxide (a commercial support produced by Condea, Chemie GmbH; UberSeering; 40; 22297; Hamburg Germany labelled as a Puralox Scca2/150 with a pore volume of 0,48 ml/g) was added to the solution to form a slurry. Impregnation and drying steps were carried out using an oil bath with conditions in Table 2.2 below.

Table 2.2: Pressure settings for the first Co/Pt impregnation

Temperature of oil bath (°C)	Rotavapor Pressure (m bar)	Time (min)
60	no vacuum	10
60	300	30
70	300	90
85	300	60
85	50	240

When the pressure decreases from 300 to 50 mbar after drying the slurry for three hours at temperatures in the range 60 - 85 °C, the wet catalyst sample became stuck on the wall of the flask. The slow drying procedure was interrupted in order to scrape the catalyst from the flask thereby ensuring homogeneous

catalyst drying. The flask in which water was collected during the drying step was emptied prior to the resumption of drying process. The quartz calcination tube with a height of approximately 50 mm was used. A quartz wool was used to prevent fine catalyst particles from entering the outlet tube, by placement into the lid of the quartz tube, through which a thermocouple was inserted to measure the actual catalyst temperature. The air supply tube was placed onto the inlet side (surgical tubing was used, although it perished quickly), and the outlet side of the calcination tube coupled to the KOH solution in the bubbler (fresh surgical tubing to be used after each experiment due to the NOx and high temperature induced rapid degradation of the tube).

Calcination was performed within an hour of impregnation end. The catalyst was calcined in a calcination tube with air at a gas hourly space velocity higher than 0.9 $m^3/kg/h^{-1}$ catalyst and atmosphere pressure. The temperature of calcination tube was increased from 250 - 272 °C and maintained at this temperature. High airflow rates were necessary for the removal of the NO_x gases evolved by the decomposition of the nitrate precursor. A representative sample produced after the impregnation and drying steps was also calcined in the furnace (Thermopower furnaces SA (Pty) Ltd) under the above conditions. After calcination step the catalyst was screened through 150 µm sieve.

The second impregnation was also performed in order to increase the concentration of cobalt and platinum in the catalyst. In this step, approximately 23.51 g of cobalt nitrate was dissolved in 40 ml distilled water and 0.039 g $(NH_3)_4Pt(NO_3)_2$ was dissolved in 10 ml distilled water. The two solutions were mixed together and transferred into a 500 ml round bottomed flask. Approximately 50 g of the recovered calcined catalyst was weighed and finally added to the nitrate solution. The catalyst was then prepared as in the first step. After calcination of the catalyst, the final catalyst was sieved to pass through 150 µm sieve. The catalyst formed was submitted for XRD and ICP-AES analyses. Following methods stated in Section 2.2, the surface area, pore volume were

measured and TPR measurements and particle size determination also undertaken. The catalyst prepared in this study could be reduced and eventually tested in a laboratory micro-slurry reactor at realistic FT conditions i.e. 220 °C, 20 bar, and 50 - 70 % conversion.

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CHAPTER 3

RESULTS AND DISCUSSION

In this Chapter, the results obtained during the valorisation of the spent catalyst, selective leaching of the calcined spent catalyst, purification of the leach liquor solution, precipitation of cobalt catalyst preparation, and characterization are presented and briefly discussed in detail. The Chapter concludes with results and discussion relevant to study of the parameters studied during the crystallisation step.

3.1. Calcination of spent catalyst

As discussed earlier in Chapter 1, the spent catalyst is significantly contaminated with hydrocarbon waxes, originating from the Fischer-Tropsch synthesis reaction. The primary aim of the calcination step is to remove the carbonaceous materials present in the spent catalyst by oxidation to the metal oxides, mainly from Co_3O_4 and SiO_2 in the acid and base-leaching step. In this Chapter, the results obtained during the calcination of the spent catalyst either in the presence of air or sodium carbonate are presented separately.

3.1.1 Calcination of the spent catalyst in the presence of air without sodium carbonate addition

Following the calcination of the spent catalyst at different temperatures (in the range 200 - 900 °C), a significant catalyst mass loss was visually observed as the flowing powder left a trace amount of the residual carbon was produced. Visual observation indicated that a black product was formed during the calcination of the spent catalyst at a temperature of 700 °C for two hours in the presence of air. A black calcined product was possibly be ascribed to the presence of cobalt species such as tetrahedrally distributed cobaltous (Co(II)) which is likely to be formed at elevated temperatures (ranging from 600 - 900 °C) (Donaldson, 2006). A blue product was obtained during the calcination of the spent catalyst at 1000 °C in the presence of air. The blue colour of the calcined spent catalyst can possibly be ascribed to the formation of the cobalt aluminate spinel at elevated temperatures. This has been suggested by Donaldson who found that the presence of the cobalt aluminate

spinel formed at high temperature is indeed blue. The diffraction patterns of the spent catalyst after calcination at elevated temperatures (700 °C and 1000 °C) are shown in Figures 3.1 and 3.2. Figure 3.1 shows that Co_3O_4 is not the only species formed when the cobalt-based FT catalyst is oxidized in air at 700 °C. The peaks at 49 and 73 degrees 2 theta suggest the co-existence of CoO.

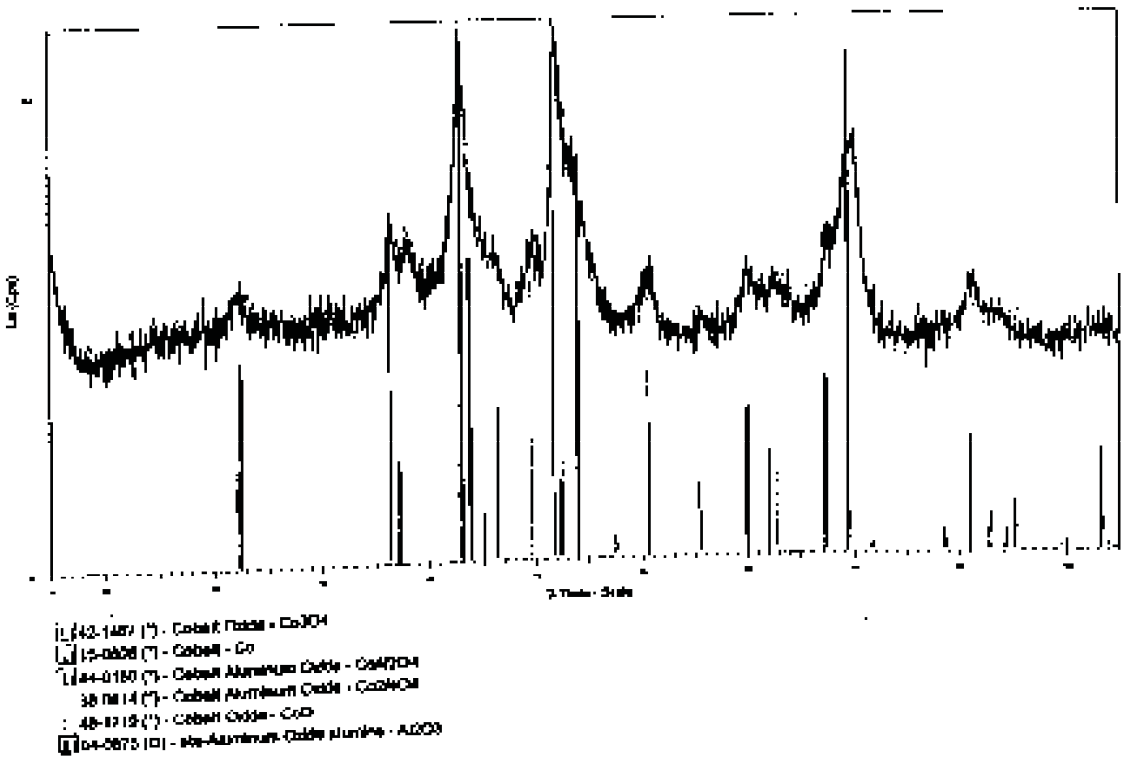

Figure 3.1: Diffraction pattern of the spent catalyst calcined at 700 °C

Table 3.1: L.O.I. results on the spent catalyst calcined at 700 °C for different times.

Time (h)	L.O.I. (%)
0	28,4
1	12,7
2	2,7
6	< 0,1

It is apparent from Table 3.1 that the L.O.I. value of spent catalyst decreases with an increase in time during the calcination step as expected. Subsequent to the oxidation of the spent catalyst for six hours period, the L.O.I. of the final oxidised spent catalyst was determined to be < 0,1 %. This implies that all of the residual carbon present in the spent catalyst was effectively removed within 6 h at 700 °C during calcination.

3.1.2 Calcination of spent catalyst in the presence of sodium carbonate

The effect of sodium carbonate on the nature of species formed during calcination of the spent catalyst was investigated. Visual observation clearly indicates that the colour of spent catalyst calcined at a temperature ranging from 700 - 1000 °C in the presence of sodium carbonate turned black. This could imply that the sodium oxide source added to the spent catalyst during the calcination step prevented the cobalt aluminate spinel formation and resulted in the formation of sodium aluminate which is water-soluble. This observation is in agreement with the results reported in the literature by Toida et al (1979) and Burnet et al (1984). It was reported that sodium carbonate can react with alumina when calcining the alumina containing feed at a temperature ranging from 600 - 950 °C to form sodium aluminate.

It is apparent from the XRD results shown in Figure 3.3 that the calcination of the mixture of sodium carbonate and the spent catalyst at 1000 °C resulted in the formation of sodium aluminate and cobalt oxide. This product was subsequently used in the leaching step in order to recover high value metals.

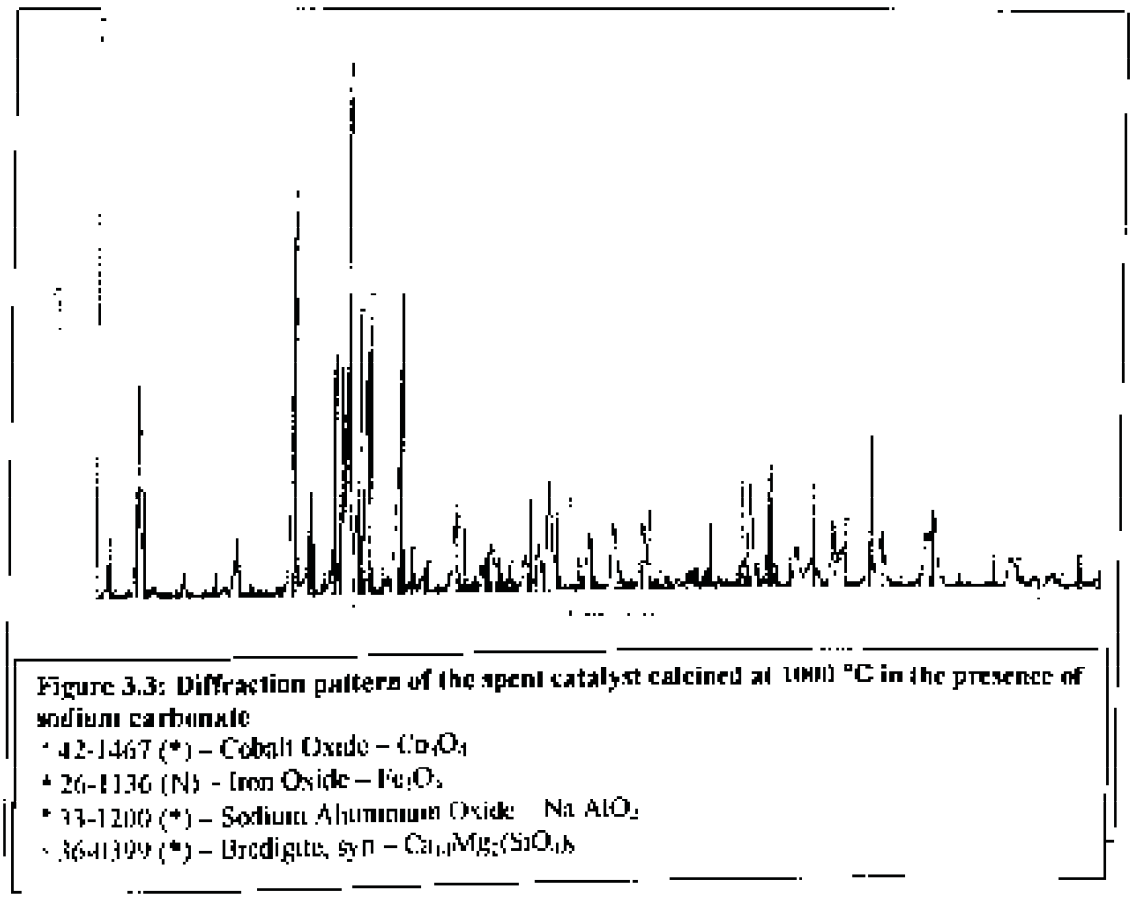

Figure 3.3: Diffraction pattern of the spent catalyst calcined at 1000 °C in the presence of sodium carbonate

* 42-1467 (*) – Cobalt Oxide – Co_3O_4
* 26-1136 (N) - Iron Oxide – Fe_2O_3
* 33-1200 (*) – Sodium Aluminum Oxide – $NaAlO_2$
* 36-1399 (*) – Bredigite, syn – $Ca_{14}Mg_2(SiO_4)_8$

3.2 Leaching of the calcined spent catalyst with the following lixiviants: NaOH, HCl, H_2SO_4, HNO_3 and H_2O

The main objective of this step is to selectively solubilise metal oxides from the calcined spent catalyst obtained during the calcination step. Therefore the metal extraction efficiencies obtained during leaching of the calcined spent catalyst with different lixiviants were carefully compared. A comparative study of the metal extraction efficiencies obtained from these different types of the lixiviants was used in order to determine which the lixiviant is suitable for the selective dissolution of the metal oxide from the calcined spent catalyst.

3.2.1 Leaching of the calcined spent catalyst with sodium hydroxide solution

The experimental procedure described earlier in Section 2.2.2 was followed to selectively dissolve alumina from the calcined spent catalyst. The results are presented in Tables 3.2, 3.3, 3.4, 3.4A and 3.5 and graphically depicted in Figures 3.4 and 3.5.

Table 3.2: Metal extraction efficiency after leaching the spent catalyst calcined at 700 °C in the presence of air with sodium hydroxide solution

Number of the leaching steps	% cobalt extracted	% platinum extracted	% aluminium extracted
1	0,18	0	75.96
2	0,25	0	89.1

Fixed conditions used during the leaching experiment : temperature 170 °C, time 4 h, pressure 9 bar and concentration of sodium hydroxide = 25 %.

Table 3.3: Metal extraction efficiency after leaching the spent catalyst calcined at 700 °C in the presence of sodium carbonate and air with sodium hydroxide solution

Number of the leaching steps	% cobalt extracted	% platinum extracted	% aluminium extracted
1	0,01	0	70,6
2	0,02	0	85,8

Fixed conditions used during the leaching experiment: temperature 170 °C, time 4 h, pressure - 9 bar and concentration of sodium hydroxide 25 %

Table 3.4: Metal extraction efficiency after leaching the spent catalyst calcined in the presence of sodium carbonate and air with sodium hydroxide solution

Number of the leaching steps	% cobalt extracted	% platinum extracted	% aluminium extracted
1	0,01	0	71,3
2	0,02	0	86,5

Fixed conditions used during the leaching experiment: temperature 170 °C, time 4 h, pressure 9 bar and concentration of sodium hydroxide 35 %,

Table 3.5: Metal extraction efficiency after leaching the calcined spent catalyst with sodium hydroxide solution

Number of the leaching steps	% cobalt extracted residue (from the residue)	% platinum extracted	% aluminium extracted
1	1,4	0	90,1
2	3,0	0	96,6

Fixed conditions used during the leaching experiment: temperature 170 °C, time 4 h, pressure 9 bar and concentration of sodium hydroxide 50 %

Table 3.5A: Metal extraction efficiency after leaching the calcined spent catalyst with sodium hydroxide solution

Number of the leaching steps	% cobalt extracted	% platinum extracted	% aluminium extracted
1	0	0	19,3

Fixed conditions used during the leaching experiment : temperature = 90 °C, time = 4 h, pressure = 1 bar and concentration of sodium hydroxide = 20 %

Table 3.6: Metal extraction efficiency after leaching the spent catalyst calcined in the presence of sodium carbonate with water

Number of the leaching steps	% cobalt extracted	% platinum extracted	% aluminium extracted
1	1,7	0	50,6

Fixed conditions used during the leaching experiment : temperature = 90 °C, time = 4 h, pressure = 1 bar.

An important point to note is that the slurry obtained during the leaching of the calcined spent catalyst with sodium hydroxide solution of different concentrations at a relatively high pressure and temperature was filtered only with difficulty. This may possibly be attributed to the formation of metal hydroxide precipitate containing ultra-fine particles during the leaching of the calcined spent catalyst at a high pH value (around 13). To further improve the filtration rate or the filterability of this slurry at an ambient temperature a suitable flocculant, which can flocculate the suspended ultra-fine materials, should be used prior to the filtration step (Adams et al. 1986 and Burkert und Hartmann, 2001).

It can be deduced from Tables 3.2, 3.3 and 3.4 that approximately 70 - 75 % of the aluminium species originally present in the spent catalyst are extracted from the calcined spent catalyst (calcined with or without the addition of sodium carbonate) when using sodium hydroxide solution (25 % w/w NaOH) after one leaching step. Table 3.2 reveals that approximately 89 % of the aluminium species present in the spent catalyst were selectively dissolved in sodium hydroxide

solution (25 % NaOH) when using an elevated pressure (about 9 bar) and temperature (170 °C) in two leaching steps.. Trace amounts of cobalt species were detected in the leach liquor solution obtained after the two leaching steps. This could be ascribed to the precipitation of soluble cobalt species from sodium aluminate solution in the form of cobalt hydroxide ($Co(OH)_2$). No platinum species were detected in the leach liquor solution. According to Warren and Hiner (1979), Hartley (1973), McDonald and Hunt (1982), Edward (1976), Habashi (1970), Renner (2001) Pt dissolves exclusively in an aqua regia medium. It is apparent from Table 3.5 that approximately 97 % of the aluminium species present in the spent catalyst were selectively dissolved in sodium hydroxide solution (about 50 % w/w NaOH) after two leaching steps. However almost all platinum species are still contained in the washed basic-residue.

From Table 3.5A it can be seen that about 19 % of aluminium species present in the calcined spent catalyst were dissolved in sodium hydroxide solution at 90 °C at 1 atm pressure after one leaching step.

3.2.1.1 Effect of temperature on metal complex solubilisation

The results obtained are graphically depicted in Figure 3.4 where it can be observed that aluminium extraction efficiency increasest with an increase in leaching temperature. During the leaching step aluminium(III) ions react with sodium ions present in the solution of sodium hydroxide to form water-soluble sodium aluminate species. In contrast, the cobalt extraction efficiency decreased as the leaching temperature increased from 120 – 190 °C. This may be attributed to the precipitation of the soluble cobalt(II) ions in the form of the cobalt hydroxide ($Co(OH)_2$), that was formed at elevated temperatures (ranging from 120 – 190 °C). This could be evidence that as water vaporised at a high temperature during the leaching, cobalt ions present in the solution react rapidly with free hydroxide ions to form a gelatinous precipitate. Visual observation indicated clearly that the colour of the solution turned blue when its temperature was increased from 27 to 190 °C. From this observation it follows that the precipitates