

Chapter 3- Results and discussion

Table 3.20: Composition of catalyst prepared by impregnating alumina with impure cobalt nitrate calcined in the furnace

Substance	Mass Percentage
	(m/m)
Fe ₂ O ₃	0,56
MnO	0,04
Cr ₂ O ₃	0,03
V ₂ O ₅	0,00
TiO ₂	0,00
CuO	0,06
K ₂ O	0,00
P ₂ O ₅	0,00
Al ₂ O ₃	76,4
SiO ₂	0,00
MgO	0,00
Na ₂ O	1,30
Cl	0,00
S	0,10
Cu	9,61
Pt	0,006
Mass Change (g)	7,52

Table 3.21: Composition of catalyst prepared by impregnating alumina with Sastech pure cobalt nitrate calcined in the calcination tube

Substance	Mass Percentage (m/m)
Fe ₂ O ₃	0,81
MnO	0,07
Cr ₂ O ₃	0,03
V ₂ O ₅	0,00
TiO ₂	0,04
CaO	0,12
K ₂ O	0,00
P ₂ O ₅	0,02
Al ₂ O ₃	67,2
SiO ₂	0,10
MgO	0,00
Na ₂ O	0,10
Cl	0,00
S	0,10
Cu	18,2
Pt	0,0589
Mass Change (g)	6,24

It can be seen from Tables 3.18 and 3.21 that the low levels of impurities such as iron, manganese, chromium, vanadium, titanium, calcium, potassium, silicon, sodium, chlorine and sulphur are still contained in both cobalt-based catalysts produced by the impregnation technique. For this technique, a commercial alumina was impregnated with pure cobalt nitrate arising from the spent catalyst. The presence of these impurities in the cobalt-based catalyst could be attributed to the presence of various impurities extracted into an organic phase during the solvent extraction method. Approximately 6 ppm of the platinum species

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were reported in the cobalt-based catalyst. The presence of this platinum species could possibly be ascribed to the trace amounts of the platinum species originating from the spent catalyst. From Table 3.17, it also follows that approximately 14.6 % Co and 70.6 % Al_2O_3 are contained in the cobalt-based catalyst. It can be seen from Table 3.21 that 18.2 % Co, 67.2 % Al_2O_3 and 0.0589 % Pt are contained in the cobalt-based catalyst originating from the spent catalyst derived-pure cobalt nitrate catalyst. The presence of the platinum species in the cobalt-based catalyst can possibly be ascribed to the tetraammineplatinum nitrate added during catalyst preparation.

It is apparent from Tables 3.20 and 3.21 that many impurities such as iron, manganese, chromium, calcium, sodium and sulphur are contained in the cobalt-based catalyst obtained during the catalyst preparation. The presence of these impurities can be attributed to the presence of the above-mentioned elements in the impure cobalt nitrate used during the catalyst preparation. It can be seen from Table 3.19 and 3.20 that cobalt-based catalysts obtained during catalyst preparation when using impure cobalt nitrate contain low cobalt content (9.45 % Co and 9.61 % Co respectively) and high alumina content (76.10 % Al_2O_3 and 76.4 % Al_2O_3 respectively). Low concentration of cobalt species and high concentration of alumina in the cobalt based catalyst produced during catalyst preparation when using impure cobalt nitrate can be ascribed to low cobalt content and high alumina content in the impure cobalt nitrate. From Table 3.18, it follows that the cobalt based catalyst obtained during catalyst preparation when using a commercial cobalt nitrate contained high cobalt content (20.2 % Co) and low alumina content (64.6 % Al_2O_3) when compared to all catalysts prepared in the experiments. It can be concluded that the commercial cobalt nitrate and pure cobalt nitrate from the spent catalyst are the most suitable for the cobalt catalyst preparation.

3.2.16.2 Surface area and pore volume of the catalyst

The analytical method described earlier in Section 2.2 was followed to prepare and subsequent characterisation of the cobalt-based catalyst. The results obtained are presented in Table 3.22 below.

Table 3.22: Surface area and pore volume of the catalyst sample

Catalyst sample	Surface area (m ² /g)	Pore volume (cm ³ /g)
1	110	0.27
2	103	0.26
3	109	0.30
4	120	0.28
5	110	0.28

- Note: 1 Cobalt catalyst prepared with commercial cobalt nitrate and tetra-ammine platinum nitrate in the calcination tube.
- 2 Cobalt catalyst prepared with pure cobalt nitrate originating from the spent catalyst and tetra-ammine platinum nitrate in the calcination tube.
- 3 Cobalt catalyst prepared with pure cobalt nitrate originating from the spent catalyst in the furnace.
- 4 Cobalt catalyst prepared with impure cobalt nitrate originating from the spent catalyst in the furnace.
- 5 Cobalt catalyst prepared with impure cobalt nitrate originating from the spent catalyst and tetra-ammine platinum nitrate in the calcination tube.

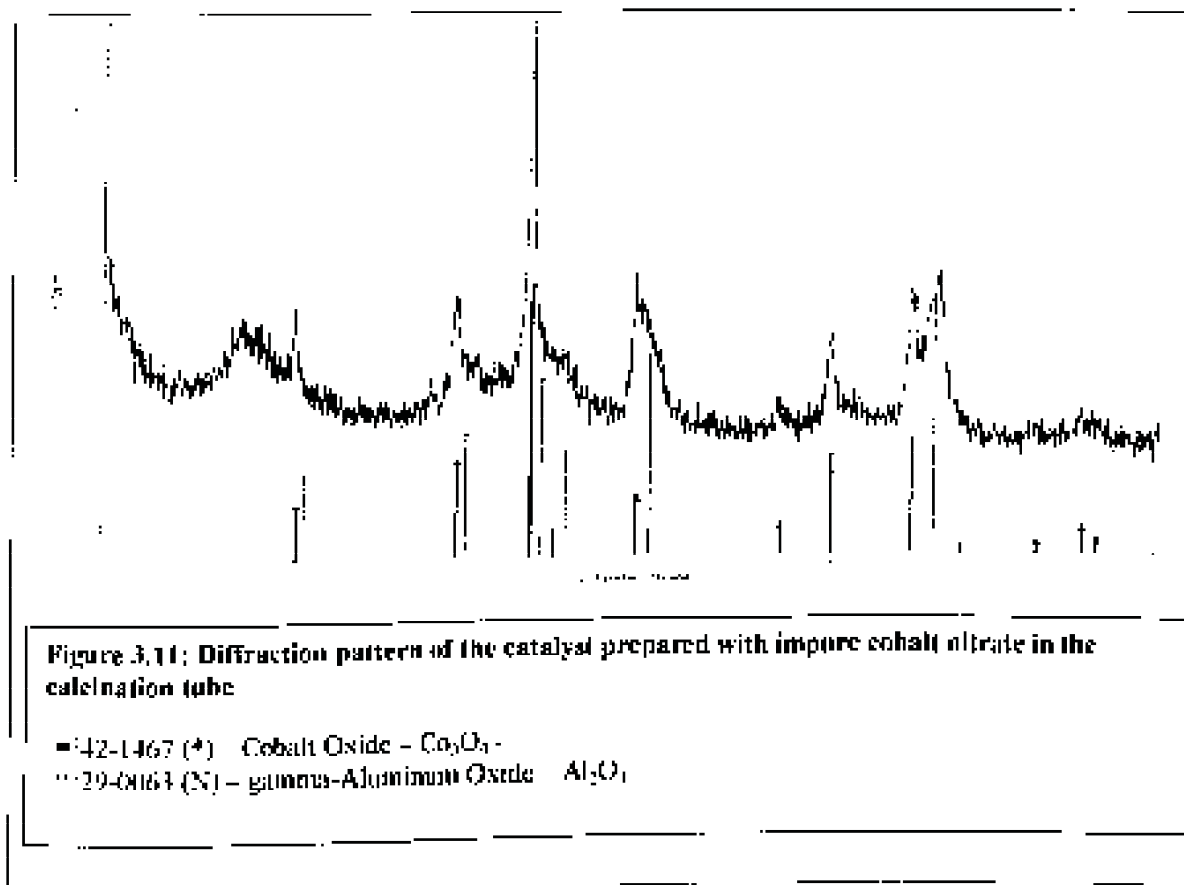
From Table 3.22, it follows that both surface area and pore volume measurements of cobalt catalyst prepared with the commercial cobalt nitrate matched those of cobalt catalyst prepared with cobalt nitrate originating from the spent catalyst.

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The surface area and pore volume of an alumina support used during the catalyst preparation was found to be 150 m²/g and 0.45 cm³/g respectively. It can be concluded that the results of catalyst obtained during catalyst preparation are lower than those of an alumina support.

3.2.16.3 XRD analysis

The analytical method described earlier in Section 2.2 was followed to prepare and characterise the cobalt-based catalyst. The results obtained are graphically depicted in Figures 3.11, 3.12, 3.13 and 3.14 below.



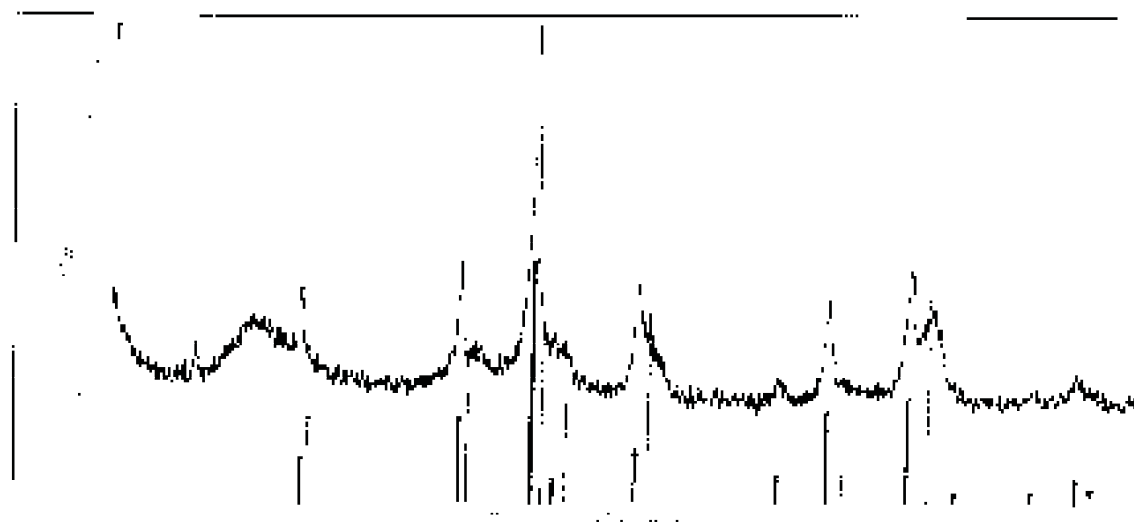


Figure 3.12: Cobalt catalyst prepared with pure cobalt nitrate originating from the spent catalyst in the furnace

■ 42-1467 (*) – Cobalt Oxide – Co_3O_4
○ 29-01063 (N) – gamma-Aluminum Oxide – Al_2O_3

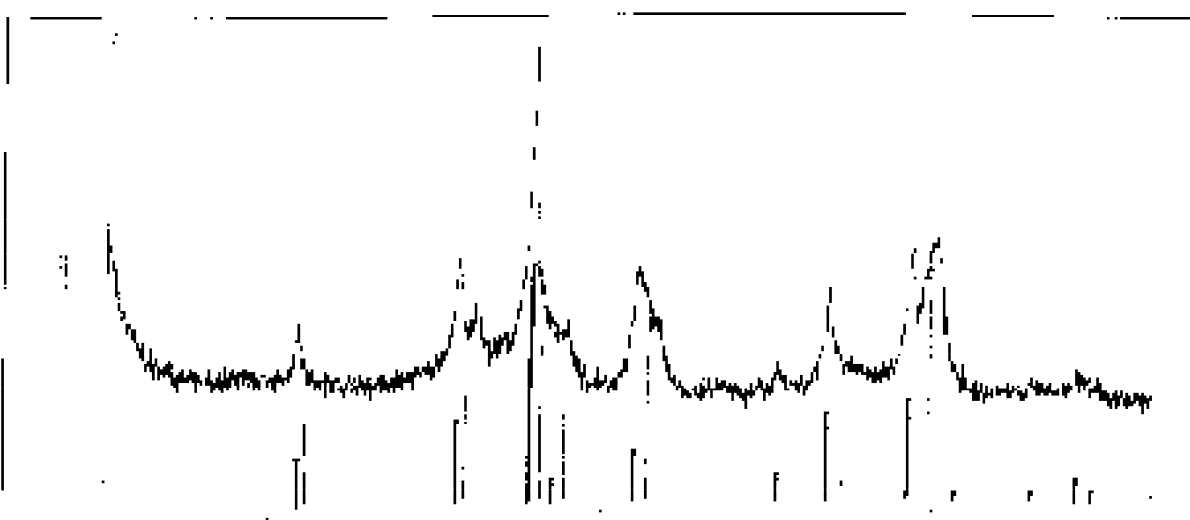


Figure 3.13: Cobalt catalyst prepared with impure cobalt nitrate originating from the spent catalyst in the furnace

■ 42-1467 (*) – Cobalt Oxide – Co_3O_4
○ 29-01063 (N) – gamma-Aluminum Oxide – Al_2O_3

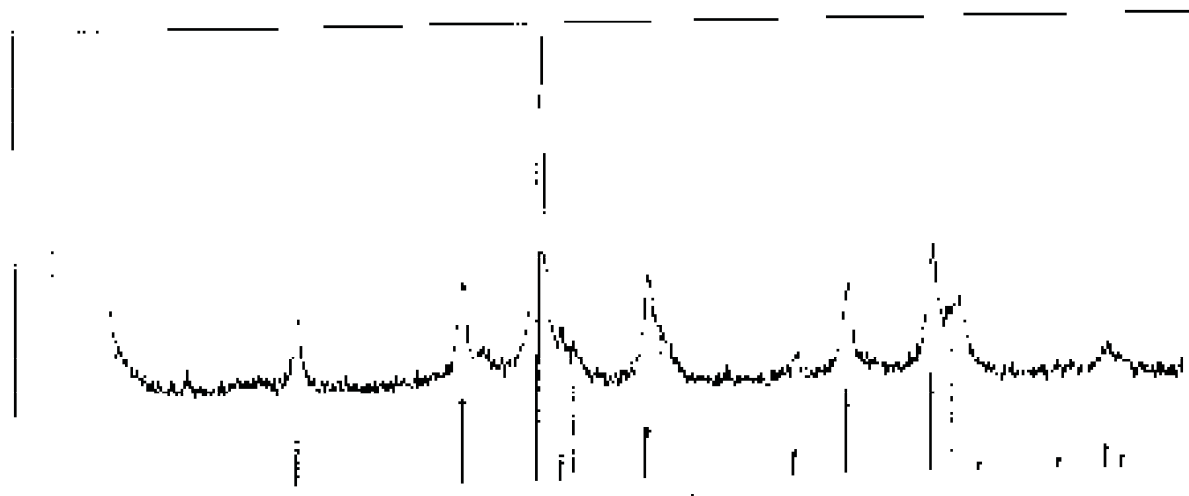


Figure 3.14: Cobalt catalyst prepared with commercial cobalt nitrate and tetraamine platinum nitrate in the calcinations tube

- 42-1467 (*) – Cobalt Oxide – Co_3O_4
- 29-0063 (N) – gamma-Aluminum Oxide – Al_2O_3

The XRD analysis indicates that both gamma alumina and cobalt oxide (Co_3O_4) are present in all catalysts prepared with commercial cobalt nitrate as well as cobalt nitrate originating from the spent catalyst. Visual observation indicates that black products were readily formed during the calcination of the alumina impregnated with cobalt(II) ions. This colour can be attributed to the presence of cobalt oxide (Co_3O_4) in the prepared catalyst.

3.2.16.4 Temperature programmed reduction

The temperature reduction results are presented in Figures 3.15, 3.16 and 3.17 below.

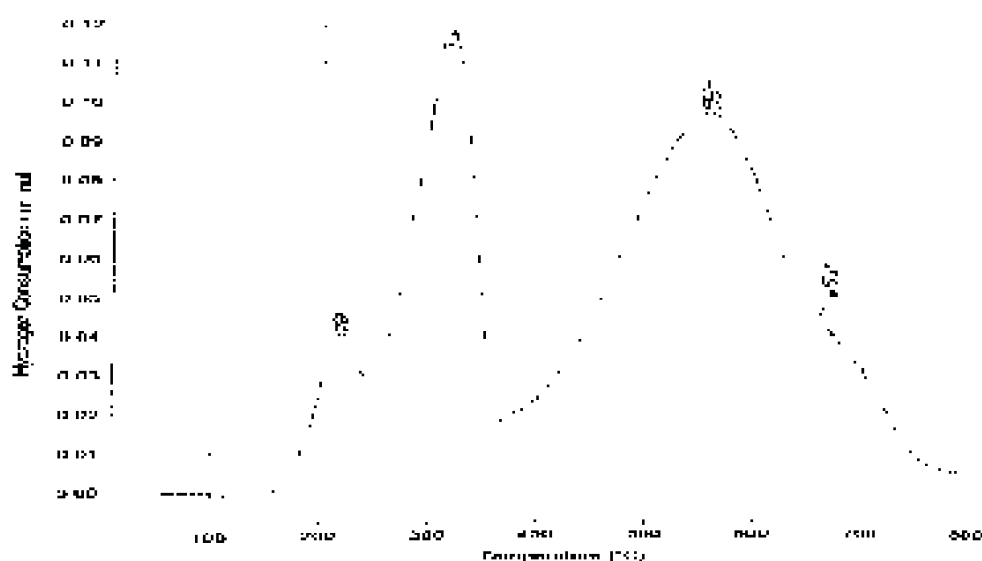
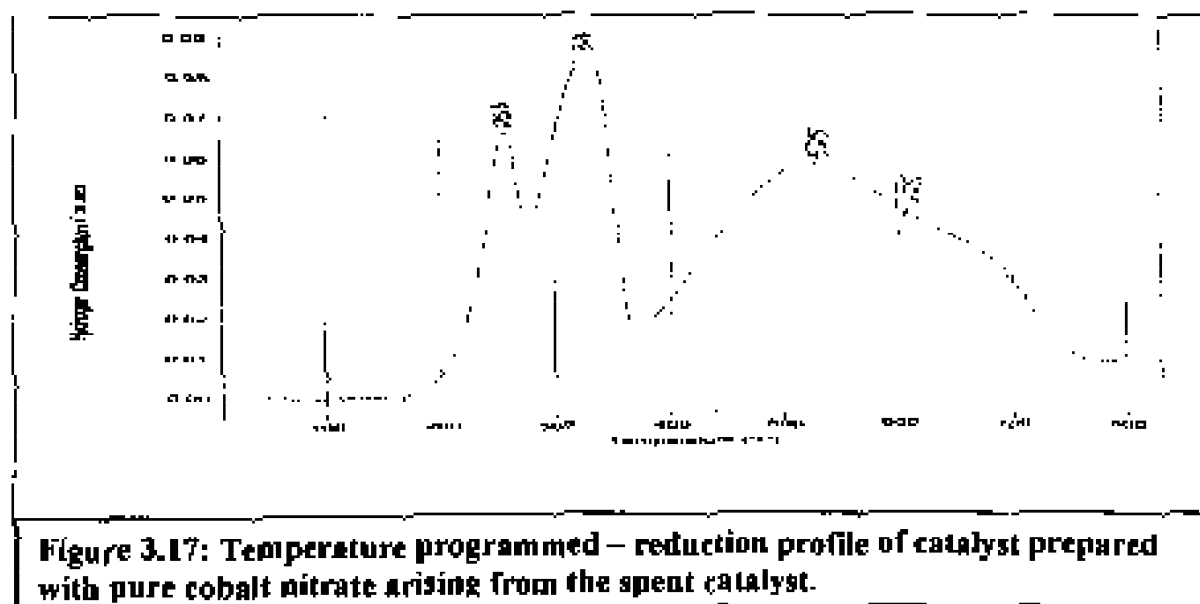


Figure 3.15: Temperature programmed – reduction profile of catalyst prepared with commercial cobalt nitrate



Figure 3.16: Temperature programmed – reduction profile of catalyst prepared with pure cobalt nitrate arising from the spent catalyst and platinum nitrate



Figures 3.15, 3.16 and 3.17 indicate the temperature-programmed reduction of the cobalt catalyst prepared with the commercial cobalt nitrate and purified cobalt nitrate originating from the spent catalyst. It can be seen from these figures that the oxides such as cobalt oxide (Co_3O_4) present in the calcination catalyst were reduced at four regions. The first peak at a temperature of between 200 °C and 250 °C indicates the reduction of Co^{3+} to Co^{2+} . The second and third reduction peaks indicate the reduction of Co^{3+} to Co^{2+} . The fourth peak reduction showed the reduction of Co^{2+} to Co metal. The assignment of the reduction of Co^{3+} to Co metal has been done by Van Schalkwyk (1998). Figure 3.15 indicates that the addition of platinum to the cobalt caused the metal ions in the oxide to reduce at a lower temperature. The second reduction peaks of the cobalt species in the presence of platinum occurred at 256 °C. The second reduction peaks for the catalysts prepared without the addition of Pt occurred at 326 °C and 316 °C. The TPR results indicate that the cobalt metal increases with an increase in temperature during the reduction of the prepared cobalt catalyst. In addition, the results suggested that the reduction of the cobalt oxide supported on alumina proceeds via a three-step reduction process. These preliminary results obtained are in agreement with those previously obtained by Maripane (2000) during the reduction of iron oxide to the iron metal. The reducibility of the cobalt catalyst prepared with cobalt nitrate and platinum supported on alumina at a lower temperature implies that the catalyst does have a slightly high mobility of oxygen at the surface. According to

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Maripane (2000) the mobility of oxygen during the reduction of the metal oxide determines the ease of reduction. The high hydrogen consumption for the second reduction step during the reduction of cobalt oxide could possibly be attributed to the reaction occurring between hydrogen and oxygen. The difference in reduction steps could imply that the catalyst formed during the catalyst preparation has different reduction potentials. From Figure 3.15 it can be seen that the lower temperature peak for the second reduction step was shifted by the presence of platinum at low temperature. It is further observed that platinum used as a promoter decreases the peak size. Furthermore, the high temperature peak was affected by promotion. It can be concluded that the reduction peaks of the catalyst arising from the commercial cobalt nitrate and pure cobalt nitrate from spent-catalysts occurred at four distinct regions

3.2.16.5 SEM analysis

SEM analysis indicated that all catalysts prepared with either the commercial cobalt nitrate or the pure cobalt nitrate originating from the spent catalyst contained some spherically shaped crystalline material (see Figures 3.18 and 3.19). The formation of this spherically shaped crystalline material could be attributed to the different dehydration factors encountered during the drying of the impregnated catalyst. The results may also indicate that the prepared catalyst consists of an amorphous material with ultra-fine particles. In addition this feature could result in the formation of the spherically shaped material with high mechanical strength during catalyst preparation.

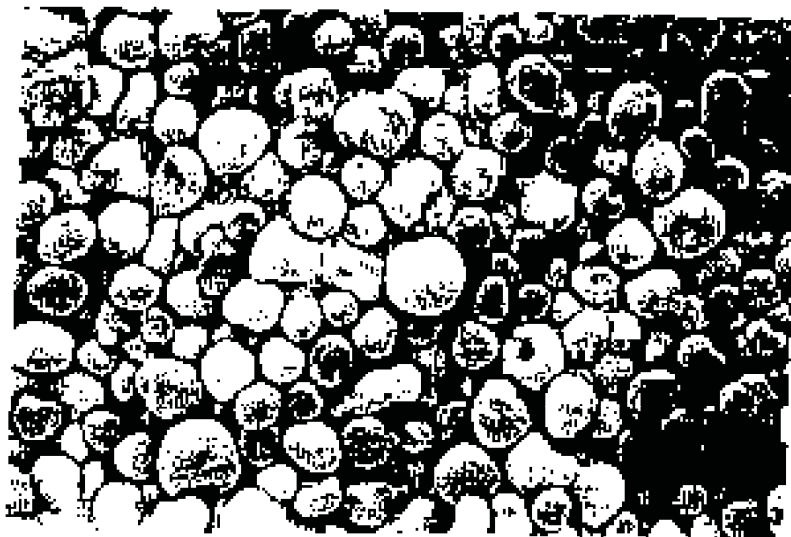


Figure 3.18 : Scanning Electron Micrograms of catalyst prepared with the commercial cobalt nitrate

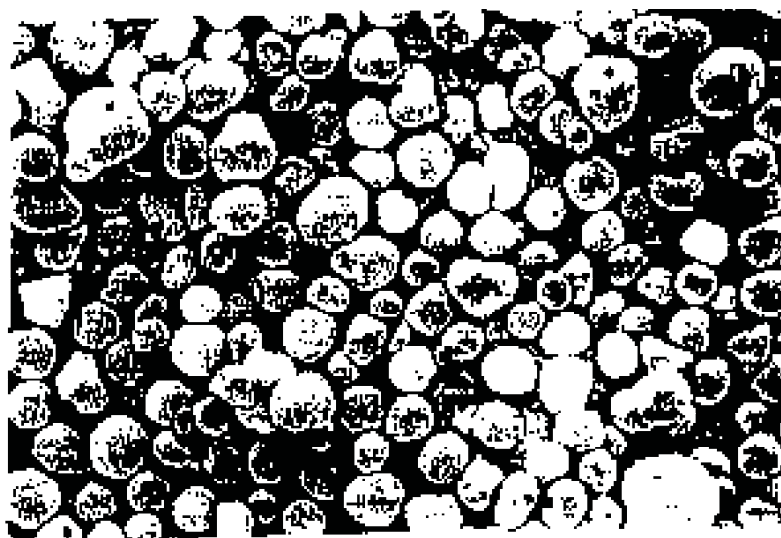


Figure 3.19 : Scanning Electron Micrograms of catalyst prepared with cobalt nitrate extracted from the spent catalyst

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CHAPTER 4

CONCLUSIONS AND RECOMMENDATIONS

4.1 Main conclusions

The main objective of this study was to use the multi-step extractive metallurgical methods to selectively recover high value metals from the spent catalyst Sasol proprietary prior to its disposal. The spent catalyst arising from the Fischer-Tropsch process typically contains carbonaceous material (60 - 70 mass %), cobalt oxide (8 -10 mass %), platinum (0.1 - 0,02 mass %) and aluminium oxide (20 - 27 %). The recovery of the valuable metal species such as platinum and cobalt from the spent catalyst could lead to a substantial profit increase and also to the elimination of the existing environmental problems associated with the disposal of cobalt. An option involving the recovery of these metals from spent FI catalysts has therefore been considered.

The results of the literature indicate that the multi-step metallurgical procedure is the most commonly used method to selectively recover valuable metals from the spent catalyst.

This method entails:

- Calcination of the spent catalyst
- Selective leaching of high value metals by inorganic acid and/or strong bases
- Flocculation and filtration of the slurry obtained
- Purification of the leach liquor solution by a solvent extraction method and subsequent selective precipitation.
- Crystallisation of the metals as salts.

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The commercial Bayer process, which involves the digestion of bauxite ore containing aluminium oxide and trace amounts of silicon dioxide with sodium (25 % m/m) hydroxide at elevated temperatures (in the range 110 – 220 °C) and pressure (in the range 4 - 20 bar) to form sodium aluminate was utilised to selectively remove alumina from aluminium containing ores. This method leads to no substantial dissolution of heavy and base metals from the spent catalysts. Under such conditions cobalt and platinum species still remain in the leached residue and were subsequently separated by treating the residue with nitric acid to give cobalt nitrate and a Pt-containing residue. The results indicate further that almost all of the aluminium species (approximately 99.8 %), cobalt species (approximately 99.8 %) and platinum species (91.7 %) that are present in the original spent catalyst were respectively dissolved in the leaching agents using the sodium hydroxide- nitric acid- aqua regia leaching process.

The detailed conclusions relating to the steps of the proposed selective recovery process are summarised in Sections 4.1.1 to 4.1.18.

4.1.1 Calcination of spent catalyst without sodium oxide source addition in the presence of air

The aim of calcining the spent catalyst was to produce carbonaceous material free calcined spent catalyst that could be used in the subsequent leaching step. It can be concluded that almost all of the carbonaceous material present in the waxy lumps of the spent catalyst was successfully oxidised at different temperatures (in the range 600 - 1000 °C) for 6 h. The XRD analysis indicates that cobalt aluminate (CoAl_2O_4) and cobalt oxide (Co_3O_4) are present in a black product formed during the calcination of the spent catalyst at elevated temperature (600 - 900 °C) in the presence of air. The spinel compounds such as cobalt aluminate and cobalt(II) dicobalt(III) oxide were also formed in the blue product during the heating of spent catalyst at 1000 °C.

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4.1.2 Calcination of spent catalyst with sodium carbonate

The main objective of calcining the spent catalyst in the presence of sodium oxide source was to form the calcined spent catalyst that contains mainly a sodium aluminate compound. This compound formed in this way was dissolved with ease in either sodium hydroxide solution or water during the leaching step. The XRD results indicate that a black product, which contains sodium aluminate and cobalt oxide, was formed during the calcination of the spent catalyst in the presence of a sodium oxide source.

4.1.3 Leaching of the calcined spent catalyst with sodium hydroxide solution

The main aim of the leaching in this study was to selectively dissolve aluminium species present in spent catalyst with sodium hydroxide solution. The results obtained during the optimisation of the leaching parameters have shown that the parameters such as temperature and time have significant effects on the extraction efficiency of aluminium species and a detrimental effect on the extraction efficiency of cobalt species during the leaching step. Approximately 89 % of the aluminium species present in the spent catalyst were selectively dissolved in sodium hydroxide solution when using an elevated pressure (about 9 bar) and temperature (170 °C) during the two leaching steps. However platinum species still remain insoluble in the sodium hydroxide solution during the leaching of the calcined spent catalyst. The leaching results also show that approximately 97 % of the aluminium species present in the calcined spent catalyst were selectively dissolved in sodium hydroxide solution (50 % w/w NaOH) at 15 bar and 190 °C in the two step leaching procedures. Trace amounts of cobalt species were detected in the leach liquor solution obtained during the sodium hydroxide leaching step. Therefore it can be concluded that the selective dissolution of aluminium species with sodium hydroxide solution (about 25 % w/w NaOH) at elevated temperature (approximately 190 °C) and pressure (12 bar) from the spent cobalt-containing catalyst was effective.

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4.1.4 Leaching of the spent catalyst with HCl solution

A solution of hydrochloric acid (about 15 % HCl) could possibly be used to selectively dissolve cobalt species with substantially no dissolution of alumina from the calcined spent catalyst. The main advantage of this option is that a pure cobalt chloride would be formed, and could be subsequently roasted at a relatively high temperature to produce a pure cobalt oxide and hydrochloric acid vapours.

During the leaching step aluminium and cobalt species present in the spent catalyst were simultaneously dissolved in hydrochloric acid solution (15 % HCl). It can be concluded that hydrochloric acid solution is not a suitable medium for the selective dissolution of these metal species from the spent catalyst.

4.1.5 Leaching of the calcined spent catalyst with nitric acid solution

The main aim of nitric acid leaching in this study was to selectively dissolve the aluminium species from the spent catalyst. It can be concluded from the results of these studies that aluminium and cobalt species dissolved simultaneously in nitric acid solution (20 % w/w) at 90 °C and atmosphere pressure.

4.1.6 Leaching of the calcined spent catalyst with sulphuric acid solution

The aim of the sulphuric acid leaching in this investigation was to selectively dissolve the aluminium species from the spent catalyst. The leaching results show that both the aluminium and cobalt species that are contained in the spent catalyst dissolved more rapidly in sulphuric acid solution to form metal sulphates, when compared with the situation found with nitric acid or hydrochloric acid. It can also be concluded that both aluminium and cobalt species dissolved simultaneously in the mineral acids such as HCl, H₂SO₄ and HNO₃. In addition, a selective precipitation method can be utilised to selectively separate the Al species from the leach liquor solution containing both the aluminium and cobalt species.

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4.1.7 Leaching of the spent catalyst with water

The aim of the water leaching was to selectively dissolve sodium aluminate formed during the calcination of the spent catalyst with a sodium oxide source. It is interesting to note that approximately 50,6 % of the aluminium species and 1,7 % of the cobalt species were selectively extracted from the spent catalyst obtained during the calcination of waxy lumps of spent catalyst with sodium carbonate when using water as a lixiviant. Therefore platinum species still remain insoluble in water. In conclusion, 99,8 % Al, 99,8 % Co and 91,7 % Pt present in the original spent catalyst were respectively dissolved in the aqueous phase during the sodium hydroxide- nitric acid-aqua regia leaching process.

4.1.8 Flocculation of the slurry samples arising from the alkaline and acid leaching steps.

Due to the presence of the ultra-fine solid particles dispersed in the leach liquor solution, a sample of slurry arising from the leaching step was filtered only with difficulty. The main objective of using the flocculation method in this study was to assist the sedimentation rate and filterability of the suspended ultra-fine solid particles from the slurry. In conclusion, the entire series of modified anionic polyacrylamide flocculants evaluated in this study can be efficiently used to flocculate the suspended ultra-fine solids from the basic slurry. Suitable operating conditions for the flocculation of the basic slurry are as follows:

- pH of the slurry in the range 11 - 12
- Concentration of the flocculant is approximately 0,25 % w/w in sodium hydroxide solution (2 % NaOH)
- Temperature of the slurry is 90 °C

From the results presented and discussed in Chapter 3, ZN92V Zetafloc was found to be a suitable flocculant for the suspended material present in the acidic cobalt nitrate containing solution.

Chapter 4 Conclusions and Recommendations

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

The aim of the acid leaching was to selectively dissolve cobalt species, which are environmentally toxic from the basic leached spent catalyst prior to its disposal. From the leaching results discussed in Chapter 3, it can be concluded that almost all of the cobalt species present in the leached spent catalyst were successfully dissolved in nitric acid solution during the leaching step. The results also indicate that almost all of the platinum species present in the leached spent catalyst still remain undissolved in nitric acid solution.

4.1.10 Platinum dissolution

The aim of the experiments was to use an aqua-regia solution to dissolve the platinum species present in the nitric acid residue. The residue was produced during the selective dissolution of the cobalt species from the basic leached residue (as described in Chapter 2). It can be concluded that almost all of the platinum species (7.7 %) present in the nitric acid insoluble residue was dissolved in aqua-regia (3HCl: 1HNO₃) at 80 °C and atmospheric pressure for 4 h to form chloroplatinic acid, H₂PtCl₆. The chloroplatinic acid formed in this manner could be used for the production of platinum metal, sponge and salts.

It is interesting to note that the blue residue, which remains undissolved in the aqua-regia solution, contains a crystalline cobalt aluminate. This by-product could be used in the ceramics and paints industries depending on its chemical purity.

4.1.11 Crystallisation of platinum from chloro-platinic acid, H₂PtCl₆

Crystallisation is one of the most common purification methods used in the chemical industry to yield a chemically pure product. Diammonium hexachloroplatinate, (NH₄)₂PtCl₆ was precipitated by reacting chloroplatinic acid with ammonium chloride. This presence of this species was confirmed by XRD analysis.

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Diammoniumhexachloroplatinate formed in this experiment could be used to prepare platinum-containing compounds.

4.1.12 Calcination of diammoniumhexachloroplatinate

The aim of the calcination of diammoniumhexachloroplatinate in this study was to produce a platinum sponge that could be used as a catalyst and also for the production of the platinum chemicals. The XRD results indicate that platinum black was formed during the calcination of diammoniumhexachloroplatinate at 800 °C in the presence of air for 1 h.

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

The main objective of this investigation was to selectively remove iron and aluminium species from the cobalt nitrate leach liquor solution via precipitation. The resultant leach liquor solution produced in this manner was used in the solvent extraction step.

From the results discussed in Chapter 3, it can be concluded that the selective precipitation of iron and aluminium species from the impure cobalt-containing solution at pH 4,5 at 50 °C was successful.

4.1.14 Purification of the filtrate produced during the precipitation step

The aim of purification of the filtrate was to produce chemically pure cobalt nitrate by solvent extraction using di-2-ethylhexylphosphoric acid as an extractant. It can be concluded that this solvent extraction method exhibited excellent performance in terms of extraction efficiency for both Co(II) and Pt(II) ions. Good phase separation was observed when di-2-ethylhexylphosphoric acid was used as an extractant and tributyl phosphate as a modifier. Subsequent to the stripping of the loaded organic phase (containing cobalt species) with nitric acid solution, a purified cobalt nitrate solution was formed. The stripped loaded organic phase could be recycled to the solvent extraction step.

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4.1.15 Crystallisation of the cobalt nitrate from the purified leach liquor solution

The XRD results indicate that pure cobalt nitrate was formed as red brown crystals during the recrystallisation of the concentrated purified and impure leach liquor solutions. The results also show that pure cobalt nitrate from the purified leach liquor solution compared favourably to the commercial cobalt nitrate in terms of chemical purity. This implies that crystallisation of cobalt nitrate from the purified leach liquor solution was successful. This compound could be used to prepare fresh catalysts for the FT-reaction.

4.1.16 Crystallisation of aluminium trihydrate (ATH) from sodium aluminate

From the results discussed in Chapter 3, it is clear that gibbsite, $\text{Al}(\text{OH})_3$, was present in both commercial aluminium trihydrate and white crystals produced during the crystallisation of aluminium trihydrate arising from the sodium aluminate solution. The ICP and XRD results also show that almost all of the aluminium ions (approximately 99 % total Al) present in the sodium aluminate solution were crystallised in the form of gibbsite.

From the results discussed in Chapter 3, it can be concluded that the product obtained during the crystallisation of the aluminium trihydrate from the sodium aluminate solution complies favourably with the specification of the aluminium trihydrate currently produced by Kynochem. This aluminium trihydrate can be used as a raw material for the production of aluminium chemicals such as aluminium sulphate, aluminium chloride, sodium aluminate and alumina. It can also be used as a catalyst support.

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4.1.17 Calcination of aluminium trihydrate to form alumina

The aim of calcination, in this study was to produce alumina from aluminium trihydrate. The alumina formed in this manner, could be used as a catalyst support in the FT catalyst. The XRD analysis shows that boehmite was formed at 400 °C whilst gamma-alumina was formed at 600 °C during the calcination of aluminium trihydrate arising from spent catalyst. It can be concluded that the alumina phase transformation observed during the calcination of aluminium trihydrate is a temperature dependent phenomenon.

4.1.18 Preparation of catalyst

In Section 3.2.16, cobalt nitrate originating from the spent catalyst was used as source of cobalt catalyst during the catalyst preparation. The cobalt catalyst produced in this manner could be utilised in the FT catalyst in order to produce hydrocarbons from the synthesis gas. The results on the cobalt-based catalyst produced from the spent catalyst derived cobalt nitrate indicated that surface area and pore volume of the cobalt catalyst prepared from the extracted cobalt is similar to that of the commercial cobalt catalyst.

The XRD analysis indicates that both gamma-alumina and cobalt oxide (Co_3O_4) are present in all catalysts prepared with commercial cobalt nitrate as well as cobalt nitrate arising from the spent catalyst.

The reduction peaks of the catalysts arising from the commercial cobalt nitrate and pure cobalt nitrate from the spent-catalysts occurred at four distinct temperature regions. The lower reduction temperatures observed with the commercial catalyst could be attributed to the presence of trace amounts of the reduction promoter, platinum.

4.2 Recommendations for further studies

The following recommendations are proposed in order to further improve the feasibility study and economic evaluation of the proposed process.

Chapter 4 Conclusions and Recommendations

4.1.17 Calcination of aluminium trihydrate to form alumina

The aim of calcination, in this study was to produce alumina from aluminium trihydrate. The alumina formed in this manner, could be used as a catalyst support in the FT catalyst. The XRD analysis shows that boehmite was formed at 400 °C whilst gamma-alumina was formed at 600 °C during the calcination of aluminium trihydrate arising from spent catalyst. It can be concluded that the alumina phase transformation observed during the calcination of aluminium trihydrate is a temperature dependent phenomenon.

4.1.18 Preparation of catalyst

In Section 3.2.16, cobalt nitrate originating from the spent catalyst was used as source of cobalt catalyst during the catalyst preparation. The cobalt catalyst produced in this manner could be utilised in the FT catalyst in order to produce hydrocarbons from the synthesis gas. The results on the cobalt-based catalyst produced from the spent catalyst derived cobalt nitrate indicated that surface area and pore volume of the cobalt catalyst prepared from the extracted cobalt is similar to that of the commercial cobalt catalyst.

The XRD analysis indicates that both gamma-alumina and cobalt oxide (Co_3O_4) are present in all catalysts prepared with commercial cobalt nitrate as well as cobalt nitrate arising from the spent catalyst.

The reduction peaks of the catalysts arising from the commercial cobalt nitrate and pure cobalt nitrate from the spent-catalysts occurred at four distinct temperature regions. The lower reduction temperatures observed with the commercial catalyst could be attributed to the presence of trace amounts of the reduction promoter, platinum.

4.2 Recommendations for further studies

The following recommendations are proposed in order to further improve the feasibility study and economic evaluation of the proposed process.

Chapter 4 – Conclusions and Recommendations

- Leaching of the uncalcined spent catalyst (original spent catalyst) with sodium hydroxide could be conducted in order to further improve the economics of the proposed process. In this study, the aluminium species could be selectively dissolved in sodium hydroxide solution. Both the platinum and cobalt species should remain undissolved in sodium hydroxide solution. The nitric acid leaching could be utilised to selectively dissolve the cobalt species from the platinum and cobalt containing leached residue. Subsequently the platinum-containing carbonaceous material would be oxidised at approximately 800 °C to produce platinum black.
- Wax extraction from the spent catalyst with xylene should be investigated in order to remove carbonaceous material prior to the leaching step. This could improve the economics of the proposed process because the preliminary calcination step could be excluded in the proposed process of recovering high valuable metals from the spent catalyst.
- In order to convert almost all of the aluminium species present in the spent catalyst to a sodium aluminate compound, the effects of the addition rate of sodium oxide to the spent catalyst, sintering time and temperature during the calcination step should be investigated. Subsequently, the leaching of sodium aluminate containing spent catalyst with various amounts of water could be conducted.
- During the characterisation of the cobalt catalyst originating from the spent catalyst, further bulk and surface properties of the catalyst could be determined using Differential Scanning Calorimetry (DSC), and X-ray photoelectron spectroscopy (XPS). These techniques could give information about the phase transitions, as well as the oxidation states and surface composition of the catalysts, respectively.

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- The final aspects that could be covered are selectivity and activity on the cobalt catalyst originating from the spent catalyst to accurately quantify the catalytic performance.