Enhanced Dispersion of Catalytic Phases on metal Oxide

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By

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Certification

This is to certify that this thesis entitled "**Enhanced Dispersion of Catalytic Phases on Metal Oxides**" submitted towards the partial fulfillment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research Pune, represents work carried out by **P.Veena** under the supervision of **Dr.P.Madhusudhan Rao** at SHELL Technology Centre, Bangalore during the academic year 2013-2014.

Coordinator, Coordinator of Chemistry Faculty

Committee:
Supervisor Name
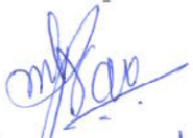Reader 1
Reader 2

Declaration

I hereby declare that the matter embodied in the report entitled "**Enhanced Dispersion of Catalytic Phases on Metal Oxides**" is the results of the investigations carried out by me at the department of CNCM, **SHELL Technology Centre, Bangalore** under the supervision of **Dr.P.Madhusudhan Rao** and the same has not been submitted elsewhere for any other degree.

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P.Veena

Signature

Thesis Supervisor: Dr.P.Madhusudhan Rao

Signature

28/3/2014

Dedicated to my Parents

Acknowledgments

I would like to express my sincere gratitude to my advisor, Dr.P.Madhusudhan Rao, for his guidance, priceless suggestions and support throughout this research. His trust and professional spirit he devoted to this work helped me in pursuing my academic goals. His encouragement has made me to become a better chemist.

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Veena,
April, 2014.

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Abstract

Enhanced Dispersion of Catalytic Phases on Metal Oxides

By
V e e n a

The aim of this Project is to investigate and optimize the rational synthesis of supported bimetallic catalysts. The main body of this work focuses on the use of simple techniques and common elemental precursors to maximize the interaction between a promoter and catalytic metal. This is achieved through the use of Enhanced Dispersion(ED) surface modification of metal oxide to increase dispersion of catalytic phases. Special attention to the surface charging parameters of oxide supports as a function of solution pH can create a driving force to selectively adsorb a precursor complex onto the surface of a support. In **Chapter 1;** a brief introduction on the relevance of studying the fundamentals of catalyst preparation is presented. **Chapter 2** gives the details of ED method used for the synthesis of supported bimetallic catalysts. **Chapter 3** discusses the details of the experiments related to FT catalysts synthesized in this study. Using ED, a simple way to increase metal *dispersion* in supported metal catalysts was discovered. From the metal uptake calculations, the optimal pH can be determined to synthesize highly dispersed bimetallic particles. **Chapter 4** discusses about the multi-gelation method to prepare high surface area Metal Oxides. **Chapter 5** focuses on the results and discussion of the work. Bimetallic catalysts were successfully synthesized for Fischer-Tropsch synthesis at different optimal pH with strong metal interaction via ED method. Clearly, the ED preparation method provides a unique basis for the addition of a second metal to increase its interaction with the active metal through simple adjustments of the preparation procedure, like precursor and solution pH.

From this work it can be concluded that the Enhanced Dispersion method leads to a selective adsorption of metal precursor onto the desired phase. Also it can lead to *highly dispersed active metal particles* on the surface of the support. By focusing on the intrinsic principles of catalyst preparation, this technique can be applied to a wide array of catalytic materials depending on the choice of the metal precursors, loading levels and choice of support etc. to increase the interaction between two metals to help improve the reactivity and selectivity of catalytic reactions.

Chapter 1

INTRODUCTORY REMARKS

1.1 At a Glance

Heterogeneous catalysis is the mainstay of chemical industry, leading to substantial advancements and innovation effectively and environmentally [1]. More than 90% of the chemical manufacturing processes in use throughout the world utilize catalysts in one form or the other [2]. The science and technology of catalysis are therefore of central practical importance.

For industrial applications, there are many methods (Wet Impregnation, Incipient Wetness(IW) Impregnation, Homogenous Deposition-Precipitation, Co-Precipitation, Chemical Vapor deposition (CVD), etc.) used to prepare a variety of metals onto high surface area supports(oxides, alumina-silicates, zeolites, etc) [3]. Out of all possible catalyst preparation methods, IW impregnation and wet impregnation are, by far, the most commonly used in preparing industrial catalysts due to their simplicity. In wet impregnation, the support material is contacted with an excess of impregnating solution and the metal precursor species may diffuse into the pore system during the equilibrium period, thus eventually leading to homogenous distribution of the metal throughout the support [4]. In contrast, in the incipient wetness impregnation, an amount of solution is applied that corresponds to the total pore volume of the support material and capillary forces provide the driving force for the imbibition of the impregnating solution into the support [5]. Overcoming years of previous use of these preparation methods and showing the effectiveness and ease of using other methods has been a challenge to researchers in the catalysis field.

It is always desired to produce catalysts which optimize cost and effectiveness. A catalyst made completely of metal would most likely have great performance, but at a substantially higher cost since only metal in contact with the reactants, either liquid or gas, would be able to participate in a reaction. Additionally, transport phenomena limitations play an important role in determining where the metal should be placed on the surface of the support[4].

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If a cluster of metal is too close to another, products produced by a specific chemical reaction will not be able to move away from the metal fast enough to let new reactants take their place. This Scenario is called "mass transport" and is a major issue in catalyst design [5]. On the other hand, placing the metal clusters too far apart would mean wastage of space and decreased overall reactivity. In both cases, the end effect is a numerically decreased reaction rate constant which would slow the conversion of one chemical species into another [5]. Keeping in mind the adage "time is money," and it is apparent that correctly spacing these metal clusters on the surface of a cheap support is most cost effective.

The degree of utilization of catalytic metal is termed as *dispersion*, the fraction of metal atoms at the surface of a metal particle divided by the total number of metal atoms. Metal dispersion and Surface area of the metal are directly related. Higher the dispersion, greater will be the surface area of the metal. Whereas the Particle size and the surface area are inversely proportional as shown in figure 1 [6]
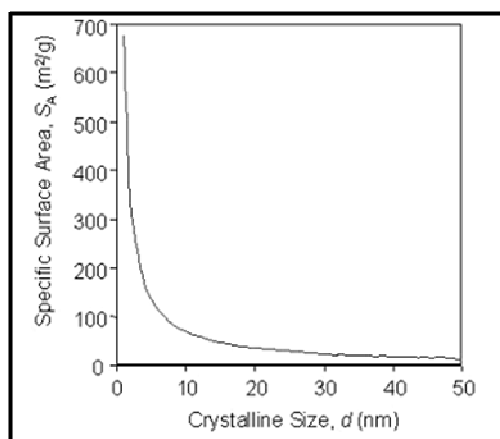
Fig.1: Specific surface area as a function of particle size [6].

Hence the goal of synthesis is to create high metal surface area or, in other words, small metal crystallites anchored onto the support. One method of producing metal supported catalysts with small metal particle sizes is through "**Enhanced Dispersion (ED)**" method.

1.2 Strategic Preparation of a catalyst

After impregnating the metal precursor solution to the support, wet slurries are dried to remove water and then heated in various oxidizing or reducing environments in order to remove the metal ligands and to reduce the metal to its catalytically active state. This sequence of steps in catalyst synthesis is illustrated in Fig.2: [7]

1) Contact solution of metal precursors with high SA support

filter or evaporate if necessary, dry

2) dried metal precursors

Δ, *calcine* (O_2), *reduce* (H_2)

3) ligands removed and metal reduced: supported metal
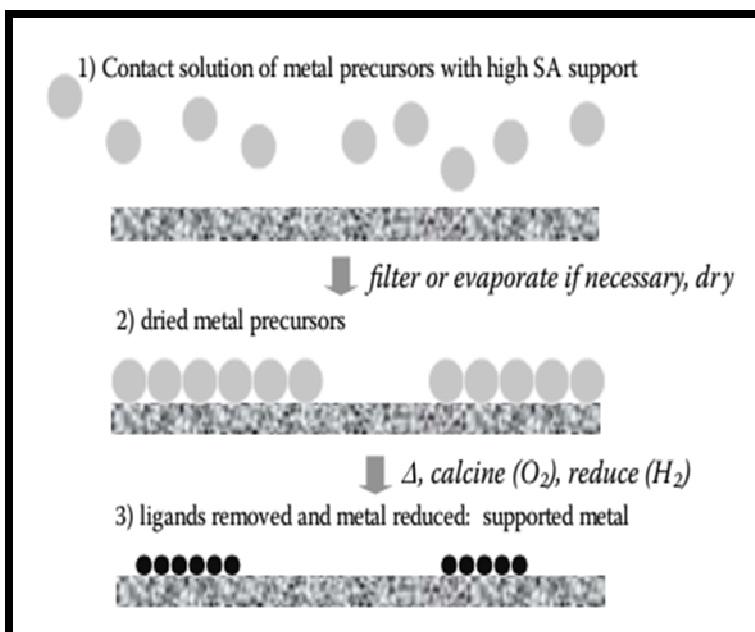
Fig.2: stages of catalyst preparation [7]

1.3 Catalytic Applications:

1.4 Fischer-Tropsch Synthesis:

$$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$$
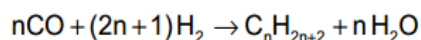
The hydrogenation of carbon monoxide is best known as FISCHER-TROPSCH (FT) Synthesis, provides an alternative to crude oil for the production of long chain liquid hydrocarbons from syngas (CO+H_2) and has been an interesting subject of development and research since the early 1930's[8]. It is also termed as GTL (gas to liquids) for the conversion of gas to liquid hydrocarbons as shown in Fig.3 [9]. Iron, nickel, ruthenium and cobalt based

materials are the classic FT catalysts, but on each type of catalyst a different product distribution is obtained. On Fe-catalysts, low boiling hydrocarbons and alcohols are the predominant products besides a great tendency towards the Water-gas shift reaction. High boiling hydrocarbons can be obtained on nickel catalysts in addition to oxygenated carbon products. On ruthenium, the formation of polyethylene was found by Pilcher [10].
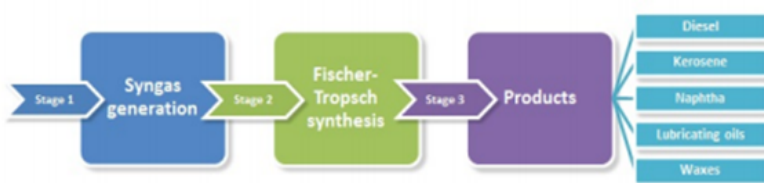
Fig.3: Simple Schematic of FT Process [9]

In the present work **cobalt catalysts** were the subject of interest. The advantages of cobalt catalysts are the absence of the water-gas shift reaction, high chain growth probability (α), the favored formation of high boiling, unbranched hydrocarbons (waxes), and barely oxygenated by-products and finally, the good availability and relatively low price [11-13]. The performance of cobalt catalysts for FT synthesis mainly depends on exposed metallic cobalt atoms [14]. Thus, a highly active cobalt catalyst requires *high dispersion* of cobalt metal. Furthermore, the present FT technology suffers from limitations in catalyst selectivity and deactivation besides the ability of the catalyst to withstand the long term adverse effects of poisoning, carbon deposition etc [15].

Hence, the main objective of this thesis was the development of a supported cobalt catalyst that distinguishes itself by a higher dispersion & lower particle size.

Chapter 2
The Nature of Enhanced Dispersion

2.1 Background

Much recent research in catalyst preparation has been focused on the "transformation of the art of catalyst preparation into a science" through fundamental studies of the adsorption process. Usually, it is believed that high activity arise from highly and uniformly dispersed active metal particles on the surface of support. In order to obtain highly dispersed active metal particles, it is necessary to know all the parameters which affect it during the preparation and after heat treatment conditions. The following parameters are taken into consideration based on literature [16]:

(1) Support: terminal OH on surface, amphoteric property, surface area and the Vacancy-defect of the core ion;

(2) Precursor: cations or anions, initial concentration, coordination chemistry in speciation of precursor;

(3) Adsorption isotherms between support and precursor;

(4) Ionic strength dependence;

(5) pH dependence;

(6) Temperature dependence in calcinations and reduction step.

2.2 The Enhanced Dispersion method, In General:

A landmark work by Brunelle in 1978 [17] presented the first evidence that noble metal adsorption onto oxides support was electrostatic in nature and qualitatively described an oxide's ability to become positively or negatively charged as a function of a characteristic pH value [18]. The concept behind this technique has been revised by Dr.John Regalbuto coined as Strong Electrostatic Adsorption method. Here after SEA will be referred to as *Enhanced Dispersion* method in this work as the latter defines the broader term. The Enhanced Dispersion method takes the advantage of a basic physical principle that opposite charges form attractive forces. Hydroxyl species present on oxide support surfaces are able to

protonate or deprotonate depending on acidity/basicity of the surrounding medium and contacting metal complexes which are oppositely charged to the support surface charge cause favorable attractions [19]. In these attractions, covalent bonding does not occur. Instead, Van der Waals forces, or "London Forces," cause the metal ion to physically adsorb to the surface.
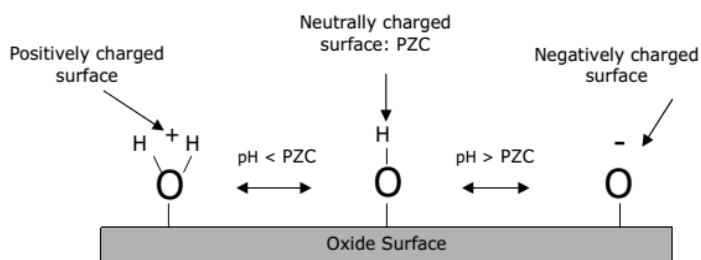
Fig.4: Schematic of Enhanced Dispersion [41]

Fig.4 shows a schematic of a surface of an oxide. As shown, at the Point of Zero Charge (PZC) of the oxide support, the hydroxyl groups on the oxide surface have a neutral charge. Ensuing protonation in an acidic environment causes the oxide support to have a positive charge thereby allowing metal ion complexes with a negative charge to strongly adsorb. Conversely, removing hydrogen in a basic environment from the oxide hydroxyl support species would allow positively charged metal complexes to adsorb strongly

The metal complex used in the project is cationic cobalt species, $Co\ (NO_3)_2.6H_2O$ [37-39] and Metal Oxide-A is considered as the oxide support. Therefore, cationic metal complexes will favorably adsorb onto supports made of Metal Oxide in basic conditions since the oxide can accrue a large negative charge. As one can imagine, the greater the absolute difference in ionic charge between the adsorbate and the adsorbent, the greater the amount of metal will adsorb. This has been corroborated in the literature to a certain extent [20-23]. However, this is not exactly the case since at extreme pH, in both the basic and acidic regions, the high ionic strength of the bulk solution causes ionic shielding effects to dominate [24]. This phenomenon is called the Deybe-Hückel effect and is well known in the field of solution thermodynamics. Therefore, while the support charge continues to accrue a greater surface charge as the pH is shifted from its neutral charge pH [25], another type of site blocking bulk solution effect acts against continued metal uptake [26]. The two effects combined form the theory for which metal uptake as a function of pH has been developed [27-28].

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After the metal is adsorbed onto the surface, the metal needs to be activated so that participation in reactions and characterization is possible. During this step, the cobalt, originally forming what is essentially a monolayer of cobalt precursor on the support surface, becomes mobile due to elevated temperature. According to entropic constraints, the cobalt molecules collide with each other to form larger structures [29]. Optimizing the parameters at which reduction occurs is therefore important in an attempt to control the outcome of this random surface motion. In some cases another pretreatment is performed before reduction, called calcination, which consists of heating in oxygen, and can assist in producing small metal particles.

## 2.3 The Enhanced Dispersion Method, To the Experimenter

For the purpose of simplicity, the Enhanced Dispersion (ED) method can be summarized in three steps.

2 Measuring PZC of an Oxide

3 Metal uptake –pH survey

4 Calcination

The first step involves no adsorbing metal. The pH of several vials of DI water is adjusted across a spectrum of possible pH values using an acid or base which will not cause catalyst poisoning. (Note: It is not important in determining the PZC of an oxide to use acids and bases which will not poison the catalyst, strictly speaking. However, it becomes important during the metal adsorption process. On the other hand, for experimental consistency it is best to use only one species of acid or base.) For Metal Oxide supports, NH_4OH and HNO_3 are good candidates for the base and acid, respectively[31-33]. HCl should not be used as the acid since chloride ions are often a catalyst poison[34]. The mass of support material in conjunction with the volume of each vial of DI water is then added individually to each sample so that high Surface Loading (SL) exists – typically around 500 $m^2 \cdot L^{-1}$– and is determined by

$$SL = \frac{(SA)(M)}{V}$$

Where SA is the surface area of the support material in units of $m^2 \cdot g^{-1}$, M is the mass of support in grams, and V is the volume, in litres, of pH-adjusted DI water to which the support is added. Agitation then occurs for 1 h at room temperature. The pH before the addition of the support material is termed the initial pH while the pH after 1 h agitation is termed the final pH. The plateau prevalent on a plot of the final pH versus the initial pH indicates the Point of Zero Charge (PZC) for the support material, illustrated in Figure 4. In the case of Metal Oxide -A support, the PZC is in the acidic range. Therefore, if cobalt is the desired metal adsorbent, the metal salt used in the next step should utilize a positive charge on the metal-containing ionic complex when dissociated [15].
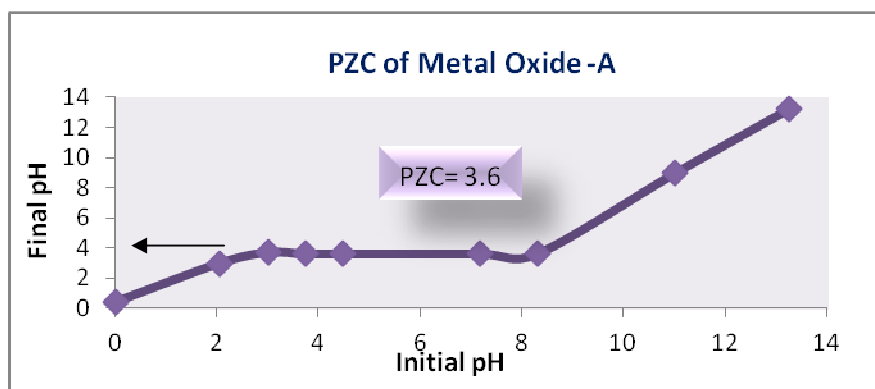
Fig.5 PZC of Metal Oxide-A

The second step is the actual survey of adsorption versus pH. A metal salt solution is first prepared at a known concentration. The pH of a portion of the solution is then adjusted using the same acid or base as in the first step. The values of the pH are chosen to survey the entire pH range. Support material is then added to each sample to maintain a SL value Agitation occurs for 1 h after which time the solutions are filtered to remove the support material. Analysis continues by evaluating the final pH of each solution and the metal content adsorbed on the support material [16]. The prepared catalysts are then dried in air .Calculation of the metal uptake follows

$$\Gamma = \frac{\left(C_{,initial} - C_{,final}\right)\ \left(mmol/L\right)}{SL\left(m^2/L\right)} \times 10^3 = uptake\left(\mu mol/m^2\right)$$

Where $C_{initial}$ and C_{final} are the concentrations of Cobalt in solution before and after 1 hr agitation with the metal in units of ppm, respectively. MW is the molecular weight of Cobalt in $g \cdot mol^{-1}$.

The third step involves calcination and reduction. For some types of supports, calcination is first accomplished by placing one of the prepared catalysts in a calcination oven. Reduction then takes place with flowing hydrogen gas at an elevated temperature. The specific parameters of the calcining and reducing step need to be optimized to yield the highest possible dispersion. For calcining, these variables include set temperature, heating duration, and ramping and cooling measures. For the reducing step, hydrogen flow rate is also a consideration.

FT Synthesis:

3.1 Outline of Regalbuto's work for FT:

Table 3.1: Experimental results of Regalbuto's work:[35]

Co loading (wt%)	Mn Loading (wt%)	Particle Size of Co_3O_4
10	1	12.5nm

*Cobalt precursor used: Cobalt nitrate $(Co(NO_3)_2.6H_2O)$

Objective: The concept behind Enhanced Dispersion technique has been revised by Dr.John Regalbuto and his work has been considered as the standard/reference for this project.

Goal of the Project

The objective of the present study is to check the feasibility of atleast doubling the cobalt content in the catalyst and maintain Co_3O_4 crystallite size based on Regalbuto's Work (ref).

3.2 Materials

Co $(NO_3)_2.6H_2O$ [37-39], Co $(acetate)_2.4H_2O$ [35], HNO_3[30] and NH_4OH [31-33] were supplied from Merck. The PZC's were measured using Regalbuto's method. Surface area was measured by using Micromeritics and the metal concentration was measured by ICP analysis before and after contacting support to determine the metal uptake.

3.3 PZC Measurements

Commercial Metal Oxides were used in this study and their properties are listed in Table 3.3.Experiments were performed on low (Metal Oxide-A) and high (Metal Oxide-C) surface area Metal Oxides. For confidential reasons, the metal oxides used as supports in this study are identified as Metal Oxide-X where X denotes the commercial suppliers. Metal Oxide -A was weighed out in order to obtain specific surface loadings for 50ml solution. Solutions were made at various pH values in the range of 1-12 using HNO_3 and NH_4OH. 50ml of each solution were added to the Metal Oxide support in 60 ml polypropylene bottles and then stirred for an hour. Final pH measurements were taken using a pH meter. The initial pH and final pH measured were then plotted with initial pH on the x-axis and the final pH on the y-axis (pH shift plots) where the plateau of the pH shift plot corresponds to the PZC of the support. PZC of different Metal Oxide supports were measured.

Table 3.3: Pertinent Properties of Metal Oxides:

	Name	Surfacearea,m^2/g	PZC
	Metal Oxide-A	48	3.6
	Metal Oxide-B	49	4
Metal Oxide Supports	Metal Oxide-C	266	8
	Metal Oxide-D	190	7.2
	Metal Oxide-E	145	5.5
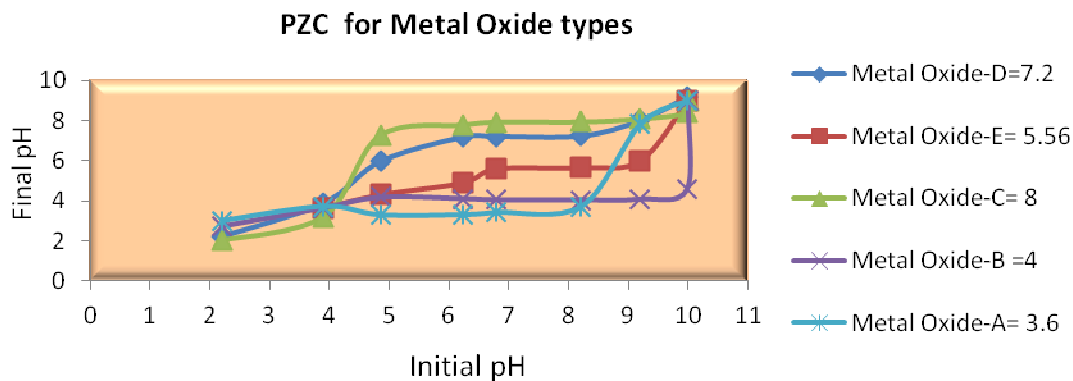
Fig.6: PZC of different Metal Oxide types

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3.4 Adsorption experiments

In order to determine the maximum cobalt uptake over Metal Oxide-A, adsorption experiments were performed at the optimal pH values for Enhanced Dispersion method. Metal Oxide -A was weighed out in order to obtain desired surface loading with 50 ml solutions. Cobalt precursor solution was made at known concentration (200ppm) by varying pH values in the range of 1-13. The initial pH values were measured and 50 ml of solution were added to the Metal Oxide -A and stirred for 1 hour. Final pH values were measured and 5 ml of slurry solution was filtered off for ICP analysis. Adsorption data is plotted with the final pH values along the x-axis and cobalt adsorption metal uptake along the y-axis as gamma ($\mu mol/m^2$).

$$\Gamma = \frac{\left(C_{,initial} - C_{,final}\right)\ \left(mmol/L\right)}{SL\left(m^2/L\right)} \times 10^3 = uptake\left(\mu mol/m^2\right)$$
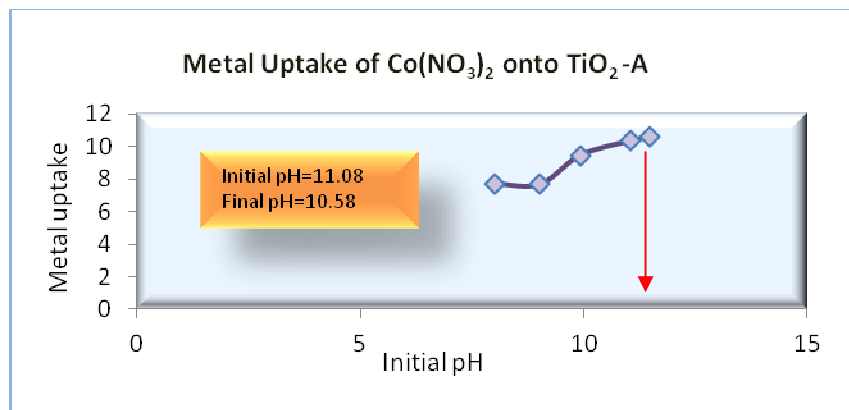
- Metal Uptake of $Co(NO_3)_2.6H_2O$ on Metal Oxide -A

Fig.7: Metal uptake of $Co(NO_3)_2$ onto Metal Oxide –A

3.5 Work Flow for the preparation of FT Catalysts - two step process:

Step-1(loading Cobalt on Metal Oxide -A):

- Measure PZC of Metal Oxide -A
- Metal Uptake of $Co(NO_3)_2.6H_2O$ or $Co(acetate)_2.4H_2O$ on Metal Oxide -A
- Loading Cobalt on Metal Oxide -A (performing the experiment)

Step-2(loading Manganese on Co/ Metal Oxide):

- Measure PZC of Co/ Metal Oxide
- Metal uptake of $Mn(NO_3)_2.4H_2O$ on Co/ Metal Oxide
- Loading Mn on Co/ Metal Oxide (Performing the Exp.)

Performing Step-1: ($Co(NO_3)_2.6H_2O$ as precursor**)**

- Measuring PZC of Metal Oxide -A
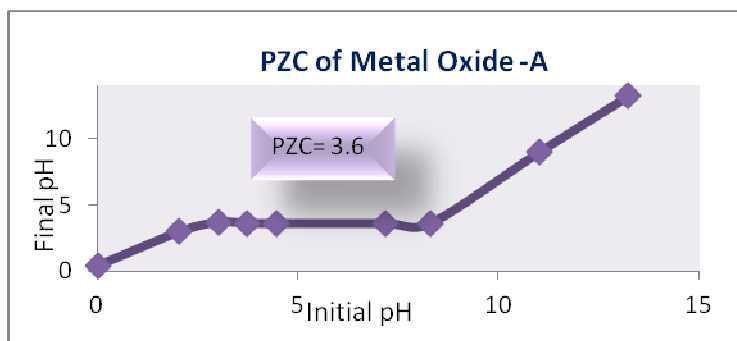
- Measuring maximum metal uptake of $Co(NO_3)_2.6H_2O$ on Metal Oxide -A

- **Loading Cobalt on Metal Oxide -A (Performing the experiment)**

  Metal Oxide -A was taken

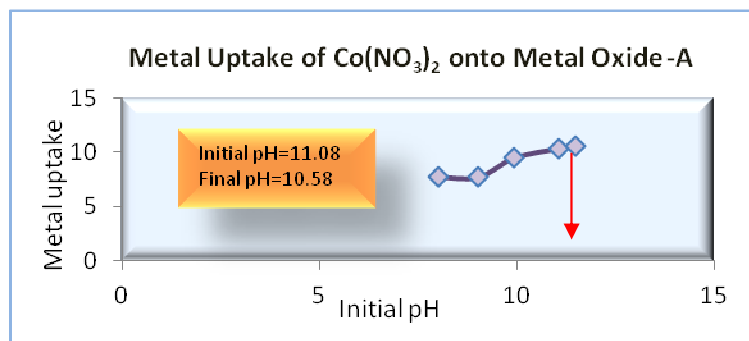 Add water to the above

  Add acid/base to the solution to maintain respective pH (11.08)

  Agitate it for 2hr

  Add Cobalt solution to it

  Stir it overnight (no heating required)

  Evaporate/Filter

  Dry in air

  Calcine in air

Step-2:
- Measuring PZC of Co/ Metal Oxide
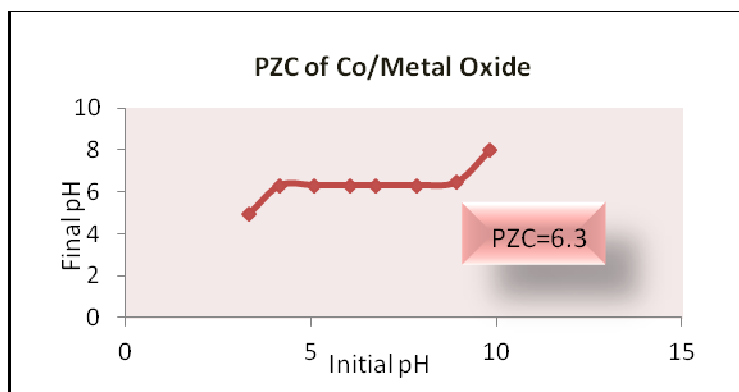
Fig.8: PZC of Co/ Metal Oxide   Fig.9: PZC-M.O., Co/MO, Co_3O_4
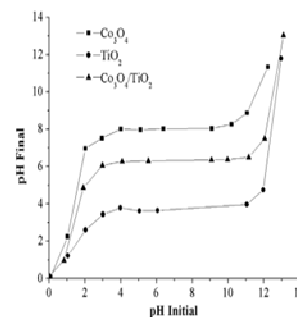
- Measuring maximum metal uptake of $Mn(NO_3)_2.4H_2O$ on Co/ Metal Oxide
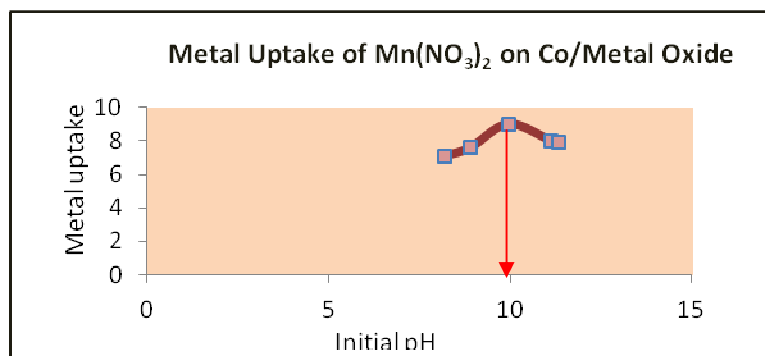
Fig.10: Metal Uptake of $Mn(NO_3)_2$ on Co/ Metal Oxide

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- **Loading Mn on Co/ Metal Oxide (performing the experiment)**

  Co_3O_4/ Metal Oxide was taken

  Add water to it

  Adjust the pH by adding acid/base to maintain desired pH

  Agitate it for 2 hr

  Add Mn solution to it

  Stir it overnight

  Evaporate/Filter

  Dry in air

  Calcine in air

- Same procedure with **$Co(acetate)_2.4H_2O$** as Cobalt Precursor
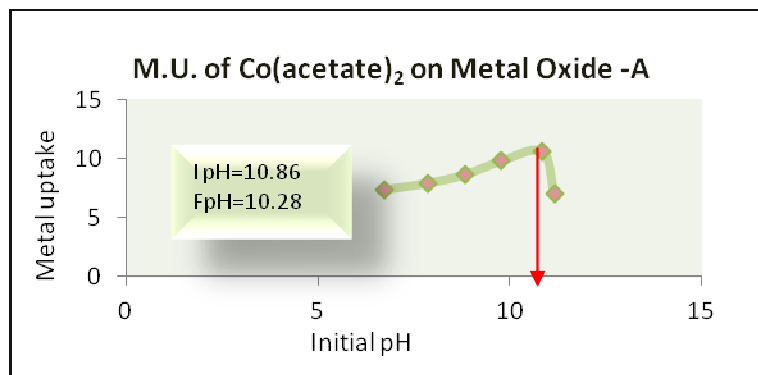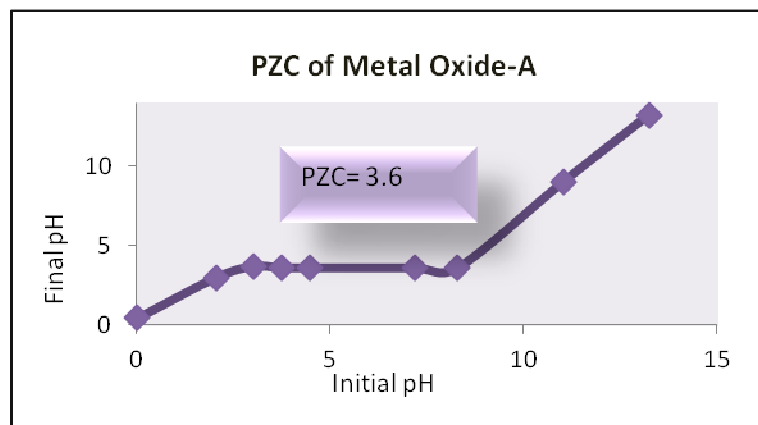
Fig.11: M.U. of Co(acetate)$_2$ on Metal Oxide -A

Mn loading on Co₃O₄/Metal Oxide
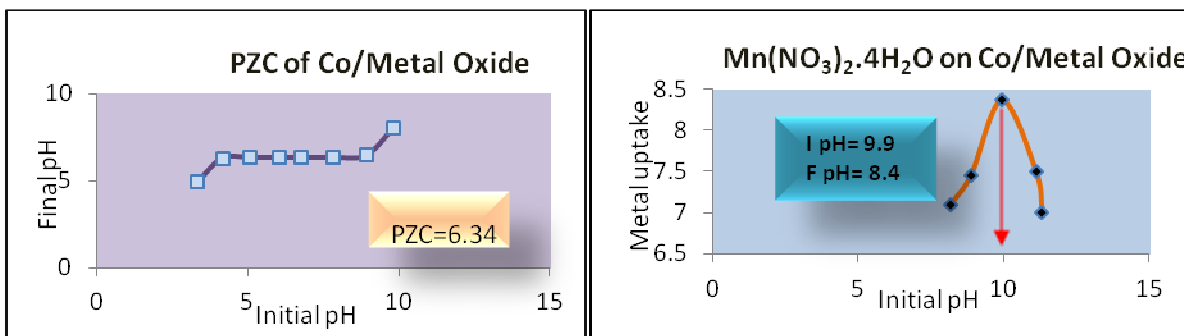
Fig.12: PZC of Co/Metal Oxide

Fig.13: Metal uptake of Mn on Co/Metal Oxide

3.6   Table: Results

Parameter	Cobalt Acetate Precursor	Cobalt Nitrate Precursor
PZC	3.6	3.6
Optimal pH	10.8	11.08
Wt% loading Co (SEM-EDX)	17	16.9
Avg.Particle Size of Co₃O₄	18-20nm	20-22nm

Experiments were done on Metal Oxides A and C; low and high Surface areas. But the Co loading onto high surface area Metal Oxide-C resulted in **amorphous Cobalt** and hence not detected by XRD. Hence, the above table gives the results of Metal Oxide-A. But the target of making **Co₃O₄** particle size ~12nm at nearly double the cobalt loading was not achieved with the aforementioned experimental procedure. Hence, design of Experiments (DOE) has been changed by varying different parameters and is termed as modified Enhanced Dispersion.

3.7 Modified ED : (Fig.14: DOE of the Project)

Metal Oxide-A

\+   (Incipient-Wetness Impregnation)

NH_4OH

Dry at 110˚C overnight   as is material

Wet Impregnation

$Co(acetate)_2.4H_2O$ $Co(NO_3)_2.6H_2O$ $Co(acetate)_2.4H_2O$ $Co(NO_3)_2.6H_2O$

Evaporated   Filtered   Evaptd   Filtrd   Evaptd   Filtrd   Evaptd   Filtrd

D- Dried only
C- Calcined

D   D+C   D   D+C   D   D+C   D   D+C   D   D+C   D   D+C   D   D+C   D   D+C

Mn $(NO_3)_2.4H_2O$ (Wet Impregnation)

Evaporation

17
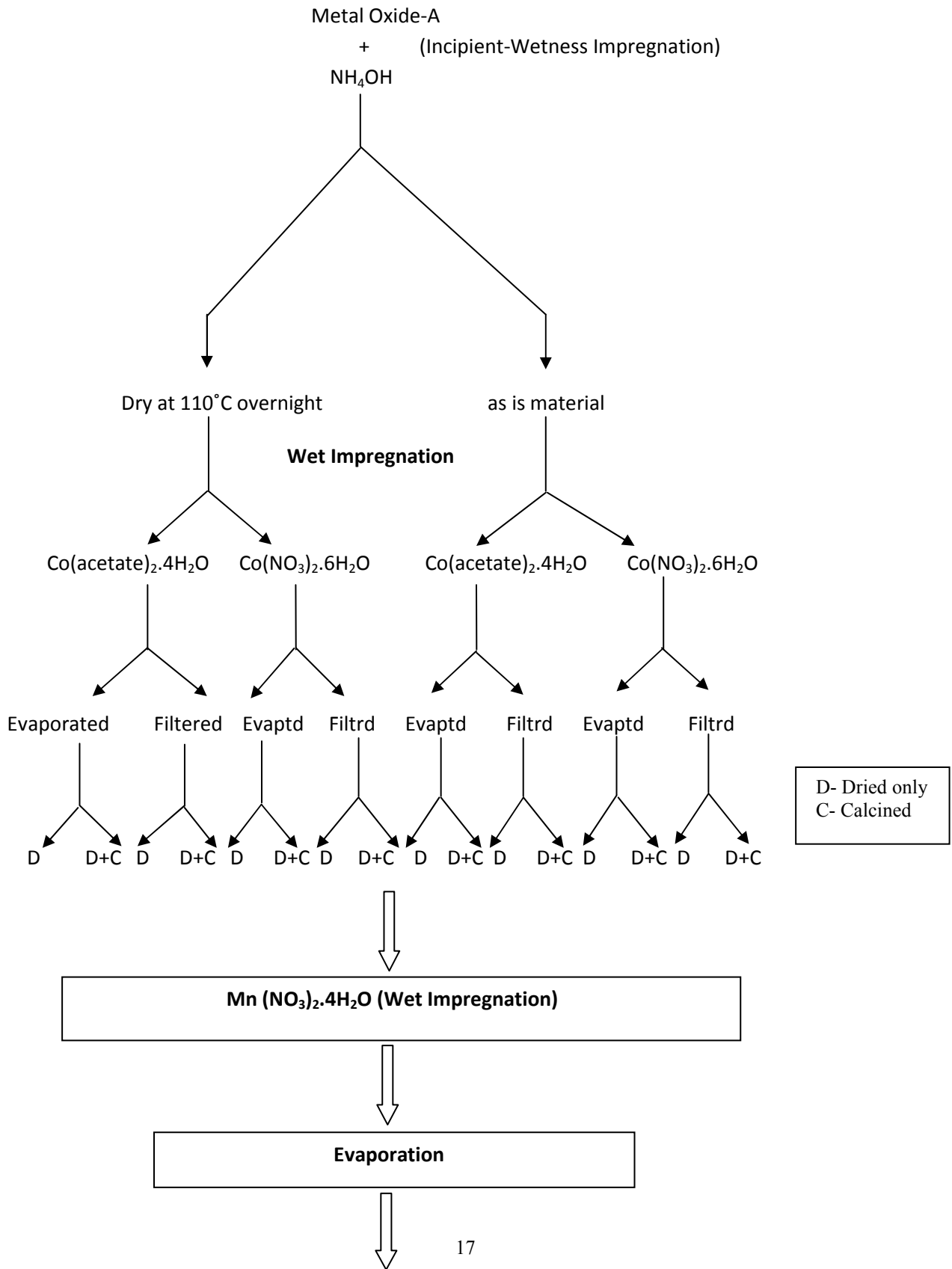
3.7a Table: Mo | **Dried+Calcined**

Sample number	Avg. Crystallite size of Co3O4 (nm) from XRD	Co loading (wt%)
1	9-10 nm	18-19
2	13-19nm	17-18
3	-	1-2
4	-	1-2
5	17-24nm	17-18
6	17-22nm	17-18
7	-	1-2
8	-	1-2
9	11-17nm	17-18
10	11-20nm	17-18
11	6-8nm	8-9
12	10-11nm	8-9
13	18-22nm	14-15
14	26-40nm	14-15
15	14-18nm	8-10
16	14-18nm	8-10

Best Result
8-10nm with **18-19wt%** loading
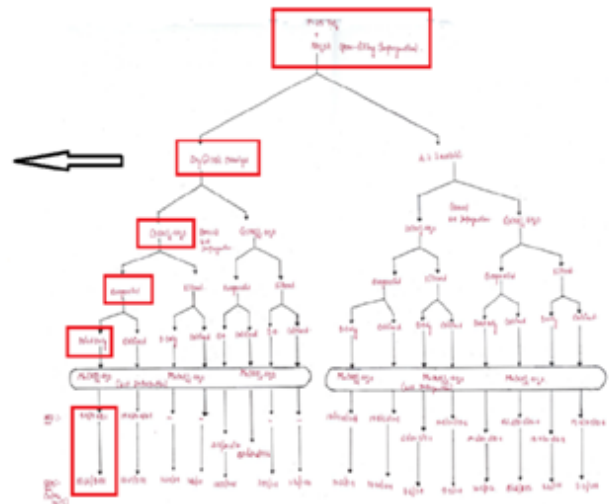
Fig.15: Best result with the experimental Plan

3.8 Experimental Procedure for the best result:

- Metal Oxide-A was taken

- The support was surface modified by filling the pores with NH$_4$OH using Incipient Wetness Impregnation.

- Agitate it for 6hr

- Dry overnight

- Co loading was done by using Wet impregnation

- Evaporated

- Dried

- Mn loading by wet Impregnation

- Evaporated

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- Dried in air

- Calcine in air

3.9 Two Solvent Technique: New Route to prepare FT catalyst [44]

- Suspension of Metal Oxide -A in Hexane ————————→Hydrophobic solution

- $Co(NO_3)_2.6H_2O + Mn(NO_3)_2.4H_2O$ in water ————————→Hydrophilic solution

- Add hydrophilic to hydrophobic solution

- Sonicate it for 30 min

- Stir it for 2 hr

- Evaporate the solvents

- Dry at overnight

- Calcine in air

3.9a.   **Table:**

Two   **Solvent**

Calcination Temperature	Co_3O_4 Particle Size

Technique Results

300˚C	22-24nm
550˚C	>30nm
700˚C	>50nm

Chapter 4

pH swing Method (multi-gelation): To prepare High Surface area TiO$_2$

4.1 Chemicals needed: Acidic TiCl$_4$, Basic Ammonia Solution.
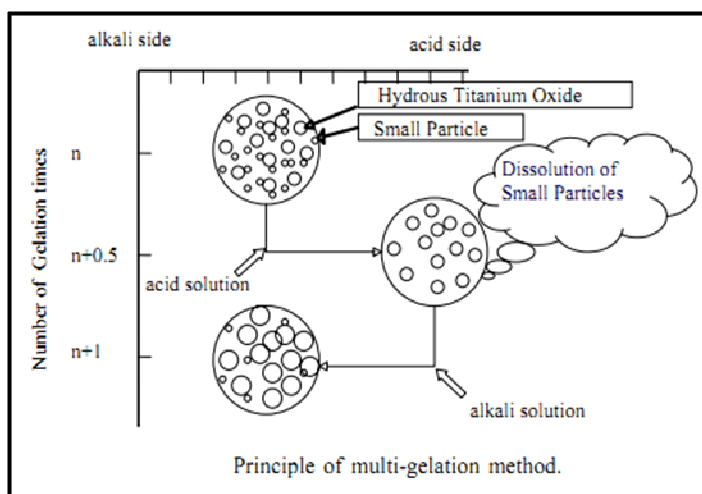
Fig.23: Principle of Multi-gelation method[36]

4.2 Experimental Procedure:

Figure above shows the principle of the multi-gelation method to synthesize TiO_2. Hydroxyl gel of TiO_2 was synthesized by swinging the pH value with $TiCl_4$ and ammonia solutions. $TiCl_4$ and ammonia solutions were supplied to the vessel alternately to prepare hydrous titanium. Particles of hydrous titanium were controlled to have desirable particle size by alternately supplying $TiCl_4$ and ammonia solution. Separated hydrous titanium was washed with water to remove ammonium chloride. After filtration, TiO_2 dried at 120°C and calcined at 500°C as the catalyst support.
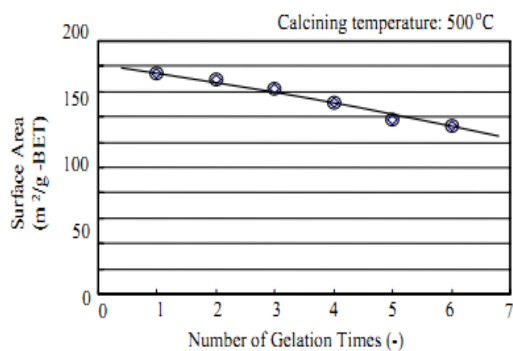
Surface area of multi-gelation TiO_2.
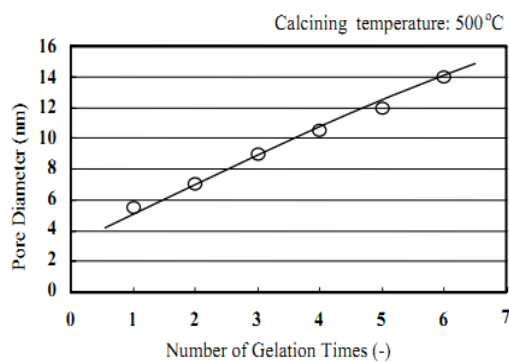
Pore diameter of multi-gelation TiO_2.
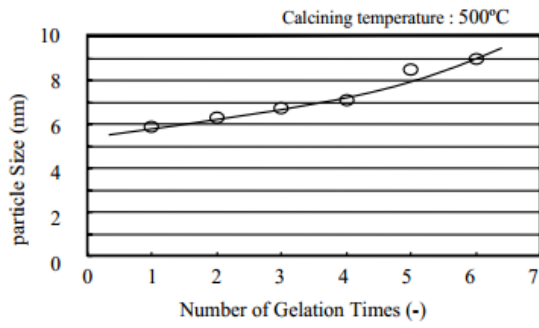
Pore diameter of multi-gelation TiO$_2$.
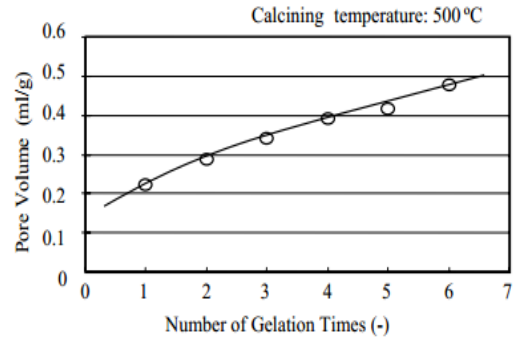
Pore volume of multi-gelation TiO$_2$.

4.3 Table: pH swing Result

Parameter	Swing number pH=8 to 2	BET surface area (m^2/g)	Pore Size(A˚)	Pore Volume(cm^3/g)
Batch-1	1	105	84	0.27
Batch-2	1	107	70	0.24
Batch-3	1	105	84	0.29

Chapter 5

Results, Discussion & Conclusion

5.1 FT:

8-10nm

Documents and Settings\galaxy\Desktop\144_009\144_048\Mn_P_25_TiO2_Co(ac)2\edsmap.spc
Chlorite (Nrm.%= 38.86, 20.96, 34.83, 1.14, 3.84, 0.28)   LSecs : 81
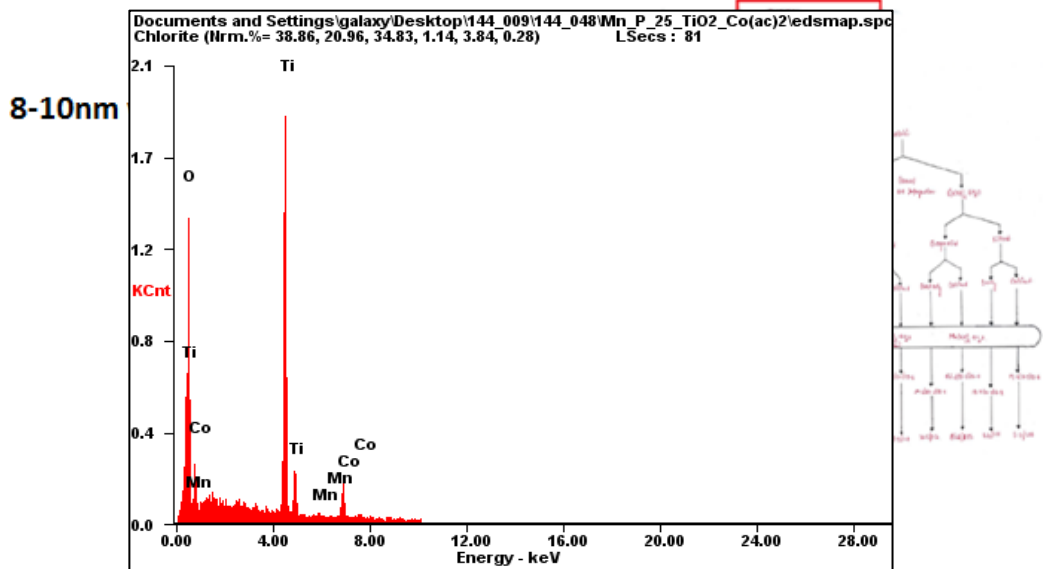
5.2 XRD: (Fig.28)
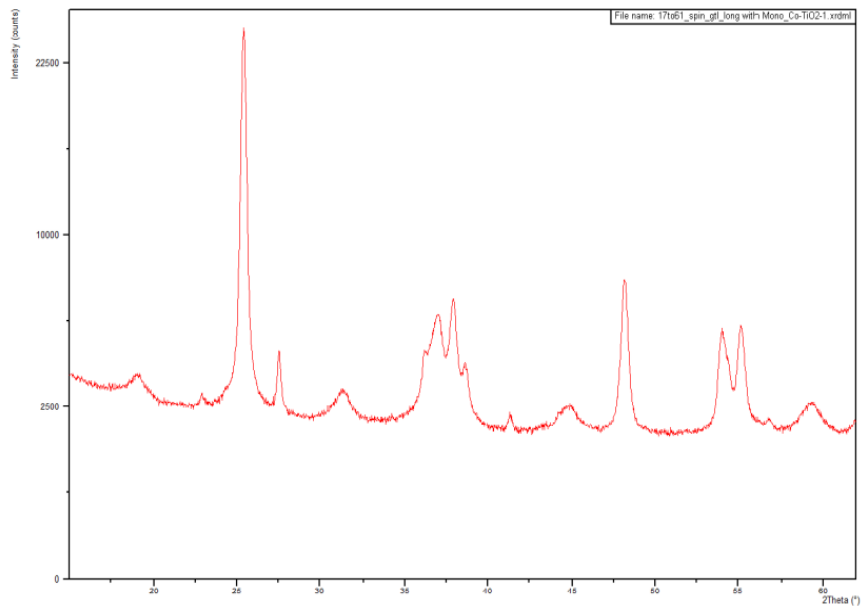
Crystalline Size: Avg.Co_3O_4 Crystallite size 8-10nm

5.3 SEM-EDX: (Fig.29)

Mapping:
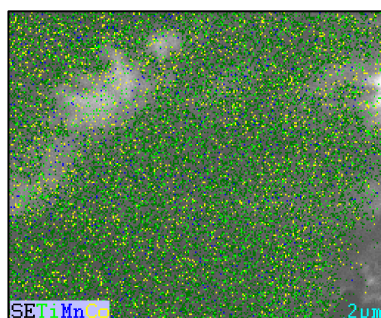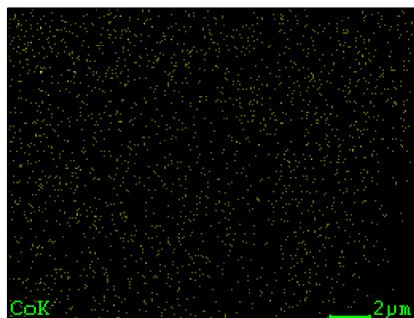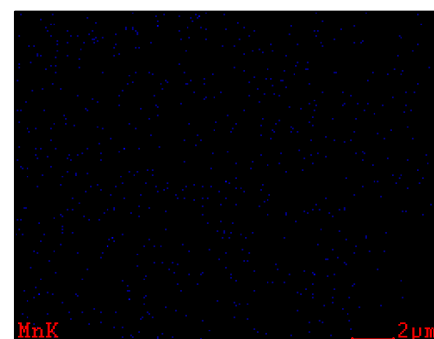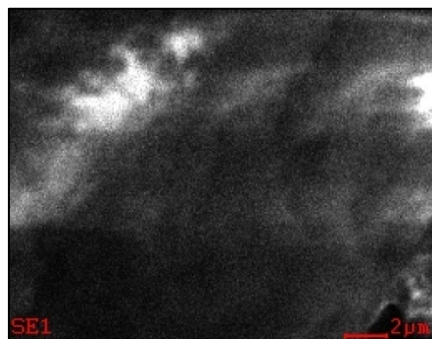
Element	Wt%	At%
OK	29.49	62.10
Metal K	51.80	31.16
MnK	**0.88**	00.47
CoK	**18.66**	06.26

Discussion:

The Experimentally-determined PZC for Metal Oxide-A is 3.6.Since this PZC lies in the acidic regime, cationic metal ions can be adsorbed, in this case, cationic cobalt like $Co(NO_3)_2.6H_2O$ and $Co(acetate)_2.4H_2O$.the pH of maximum cobalt uptake was determined to be 11.08 for nitrate complex and 10.80 for acetate precursor. Figure.28 shows the results of XRD analysis for the best result. Using Scherrer equation, crystallite size of metal can be measured and the average particle size of Co_3O_4 is 8-10nm.Figure.29 shows the SEM images for the sample. The intensely yellow colored, smaller objects which appear to be speckled are cobalt particles in the catalytically active state. The material on which they lay is Metal Oxide-A support (green colored). Dark regions show an absence of material. As aforementioned, dispersion is a measure of the particle diameter and is therefore a function of the spacing of the metal particles on the support surface. Mapping images exhibit high dispersion since the cobalt particles are very small and are densely spaced. EDX data shows the loading of Co in the sample (table given above) with 18-19wt% Co.

5.4 Conclusion:

- Surface charge of Metal Oxide can be tuned by inducing the electrostatic interactions between the active phase and the support
- Conventional ED is proven to achieve high dispersion at low metal loadings but requires optimization for achieving high dispersion at high metal loadings.
- To increase the dispersion using ED, organic source of cobalt (cobalt acetate) has to be used. But the cost of the precursors (too high) will be a limiting factor from the commercial standpoint.
- Conventional ED (without modification) cannot be used for inorganic precursors (nitrate complexes) at high metal loadings to achieve high dispersion.

5.5 Two Solvent for FT: (XRD data)

Calcination Temperature	Co_3O_4 Particle Size
300°C	22-24nm
550°C	>30nm
700°C	>50nm

Discussion:

The goal of the present study was to define mild reaction conditions to efficiently use the porosity of a Metal Oxide support as a nanoreactor to grow cobalt nano wires. After the samples are loaded with Cobalt and Manganese complexes, the Co-loaded Metal Oxide A samples have a light color, ranging from pink to light brown. At a molecular level, pH conditions used are near to 5.5 whereas the Point of Zero Charge (PZC) of Metal Oxide -A is 3.6, where surface hydroxyl groups are deprotonated. This generates negative charge that induces electrostatic interactions with the cationic Co & Mn precursors.XRD analysis suggests that the materials prepared using this technique didn't give satisfactory result of < 10nm particle size of Co_3O_4. Calcining the samples at different temperatures gave different results. A trend was noticed between the particle size and the calcination temperature. With increase in temperature from 300°C to 700°C, particle size obtained increased drastically. This is due to a deactivation mechanism called "**sintering**" which occurs at elevating temperatures leading to the formation of Co_3O_4 clusters and so increases the crystallite size of Co_3O_4 at high temperatures.

5.6 Conclusion:

- Using Two Solvent Technique, desired particle size is not achieved.
- With increase in temperature, particle size is increased due to "**Sintering**" of Co_3O_4 particles (cluster formation).

5.7 pH swing Method:

Result: BET Surface area (Micromeritics)

Fig.32 Batch-I: Summary Report

Summary Report

Surface Area

Single point surface area at p/p° = 0.200692217: 100 .6276 m²/g

BET Surface Area: 104.9630 m²/g

Langmuir Surface Area: 145.9226 m²/g

t-Plot External Surface Area: 107.3844 m²/g

BJH Adsorption cumulative surface area of pores
between 17.000 Å and 3000.000 Å width: 113.216 m²/g

BJH Desorption cumulative surface area of pores
between 17.000 Å and 3000.000 Å width: 129.1989 m²/g

Pore Volume

Single point adsorption total pore volume of pores
less than 1081.076 Å width at p/p° = 0.981918223: 0. 264516 cm³/g

t-Plot micropore volume: -0.002232 cm³/g

BJH Adsorption cumulative volume of pores
between 17.000 Å and 3000.000 Å width: 0.272821 cm³/g

BJH Desorption cumulative volume of pores
between 17.000 Å and 3000.000 Å width: 0.272115 cm³/g

Pore Size

Adsorption average pore width (4V/A by BET): 100.8034 Å

BJH Adsorption average pore width (4V/A): 96.390 Å

BJH Desorption average pore width (4V/A): 84.247 Å

Fig.33 Isotherm Linear Plot:

Fig.34 BJH Desorption- Pore volume:

28

Fig.35 BJH Desorption-Pore size:
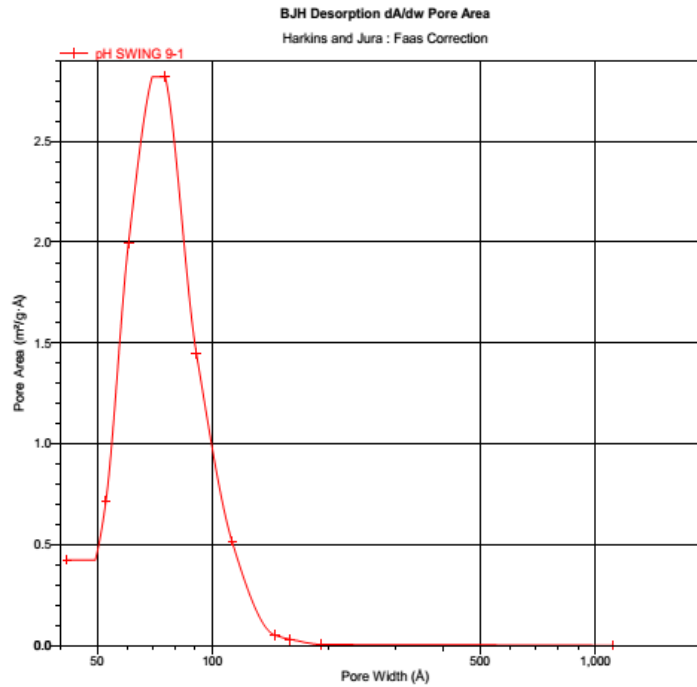
Fig.36 Batch-II: Summary Report

Summary Report

Surface Area

Single point surface area at p/p°= 0.200258902: 102.8085 m²/g

BET Surface Area: 107.2614 m²/g

Langmuir Surface Area: 149.1959 m²/g

t-Plot External Surface Area: 108.0667 m²/g

BJH Adsorption cumulative surface area of pores
between 17.000 Å and 3000.000 Å width: 117.636 m²/g

BJH Desorption cumulative surface area of pores
between 17.000 Å and 3000.000 Å width: 138.2328 m²/g

Pore Volume

Single point adsorption total pore volume of pores
less than 3953.129 Å width at p/p°= 0.995141848: 0.253143 cm³/g

t-Plot micropore volume: -0.001554 cm³/g

BJH Adsorption cumulative volume of pores
between 17.000 Å and 3000.000 Å width: 0.255892 cm³/g

BJH Desorption cumulative volume of pores
between 17.000 Å and 3000.000 Å width: 0.242677 cm³/g

Pore Size

Adsorption average pore width (4V/A by BET): 94.4025 Å

BJH Adsorption average pore width (4V/A): 87.012 Å

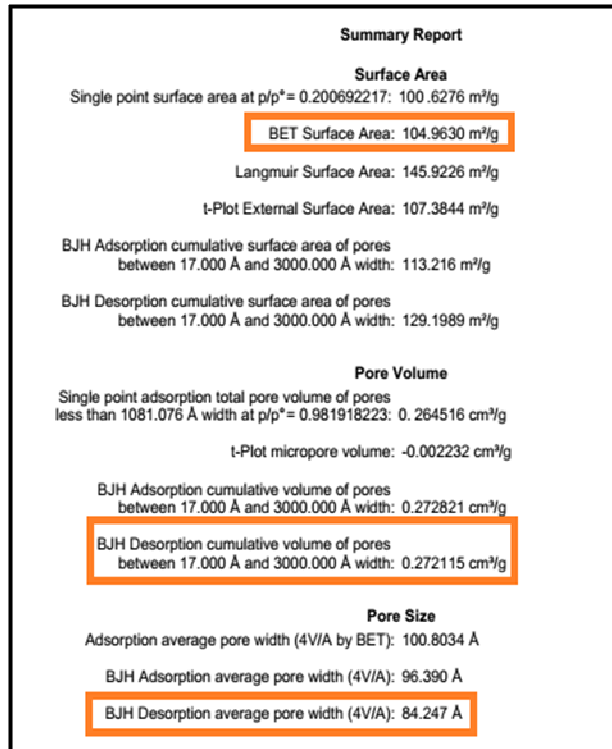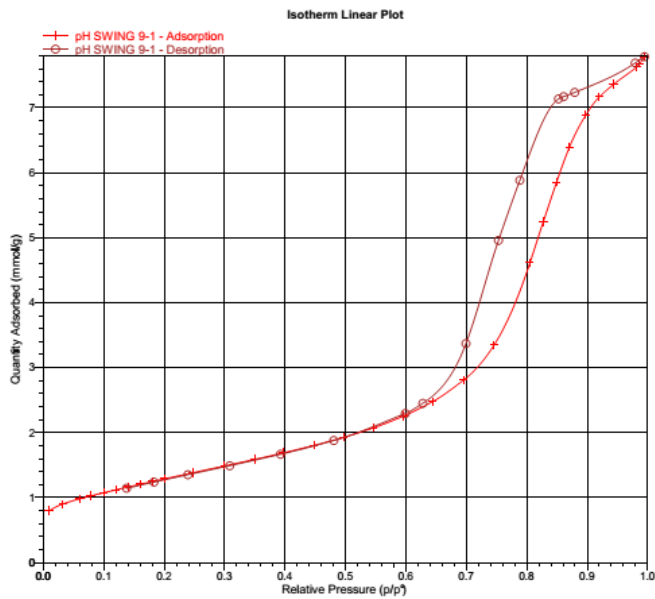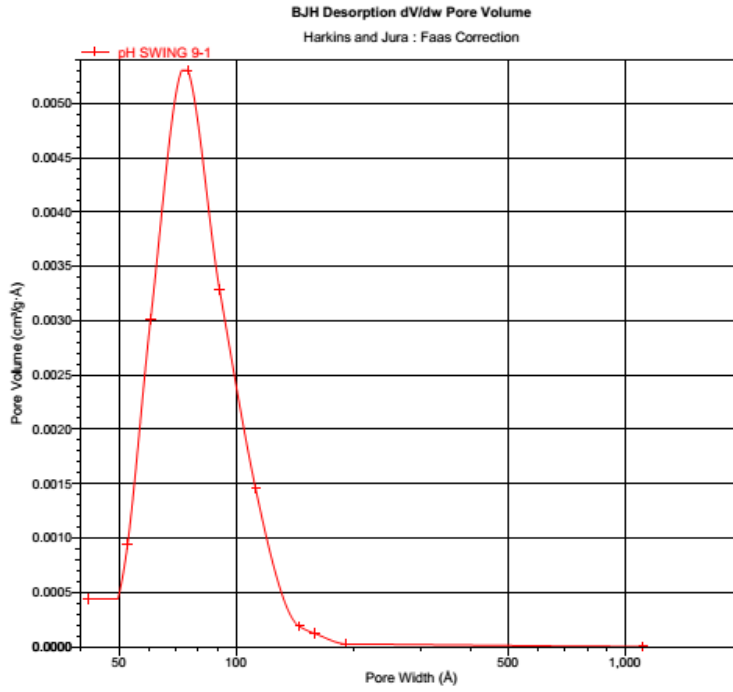BJH Desorption average pore width (4V/A): 70.223 Å

Fig.37 Isotherm Linear Plot:

Fig.38 BJH Desorption- Pore volume:

BJH Desorption dV/dw Pore Volume
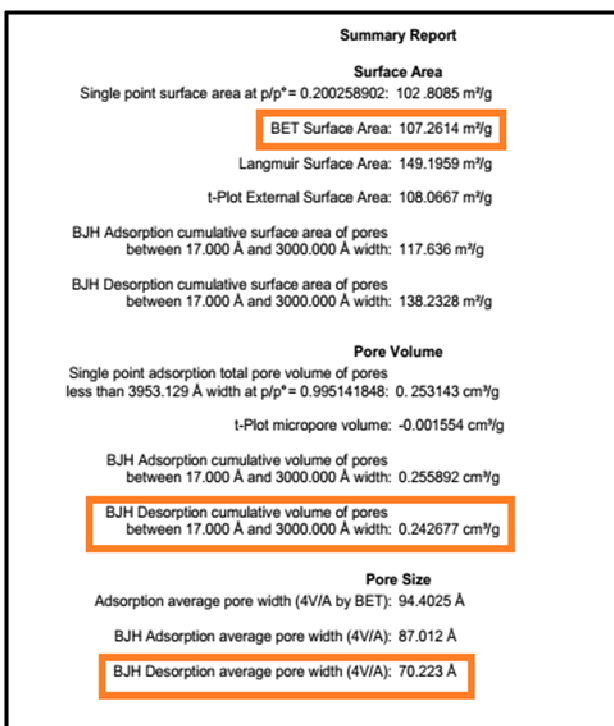Harkins and Jura : Faas Correction

Fig.39 BJH Desorption-Pore size:

BJH Desorption dA/dw Pore Area
Harkins and Jura : Faas Correction

Result:

Parameter	Swing number pH=8 to 2	BET surface area (m²/g)	Pore Size(A°)	Pore Volume(cm³/g)
Batch-1	1	105	84	0.27
Batch-2	1	107	70	0.24
Batch-3	1	105	84	0.29

Discussion:

Figure shows the magnified image of piece of porous inorganic oxide. As for pore structure, basic physical properties, such as particle size, pore diameter, pore volume and specific surface area are determined by the constitution of primary and secondary particles. The pore structure is created by the coagulation of the primary and the secondary particles.
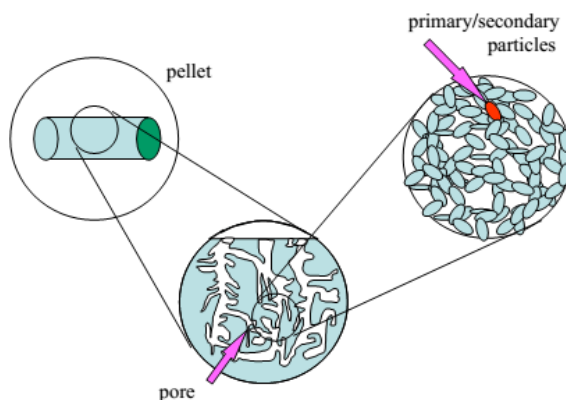
With increase in gelation times, the particle size increases. As particle size became larger, its pore size and pore volume became larger and the specific surface area was decreased. On the contrary, as particle size became smaller, pore diameter and pore volume were smaller while specific surface area increased. Results of Specific surface area and the pore properties of Titania support produced by multi-gelation method are given in the table above.

6.9 Conclusion:

- Two fold high Surface area was obtained in comparison with conventional Metal Oxides
- Reproducibility was confirmed.

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