"Synthesis and characterization of bulk and supported nickel catalyst precursor"

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Abstract:

The experimental series described here is a simple way of explaining the concepts involved in the preparation of catalytic precursors for nickel such as NiO and NiO-Supported ober $NiAl_2O_4NiO$ both stoichiometric and non-stichiometric compounds are prepared. Carbonate method gives stoichiometry while nitrate and oxalate method gives non stoichiometricNiO. Supported NiO samples are prepared by incipient impregnation wetness method. The compositional study of such precursors is done by comlexometric titration.

Keywords:stichiometric, catalytic precursors, Carbonate method,   incipient impregnation wetness method.

Introduction:

Bulk and supported nickel catalyst are widely used in heterogeneous catalysis in reactions such as hydrogenation, Oxidation, etc. NiO(non stoichiometric) is used as bulk precursor. NiO(non stoichiometry) make it catalytically active.The reference related to simple synthesis and characterization of several nickel catalytic precursors is an experiment for advanced inorganic chemistry courses. Based on this article the present project was carried.The paper named simple synthesis and characterization of several Nickel catalyst precursors, describes method for prepration of NiO samples supported on R- Al2O3 and NiAl2O4 (Impregnation wetness method), characterization of precursor NiO, NiO-NiAl2O4 and NiO-r-Al2O3 by XRD. TPR and SEM. Leads to some conclusions as follows:

NiO(A)	NiO-r- Al2O3 (B)	NiO-NiAl2O4 (C)
XRD 1) More crystalline NiO 2) Size of NiO is greatest	Least crystalline NiO size of NiO is smallest	Less crystalline NiO size of NiO is intermediate.
TPR 1) One step reduction	Two step reduction	Three step reduction
SEM 1) Particle size 300nm. 2) ---	Amorphous surface. Interaction of NiO with support.	Particle size is smaller than 100nm. Interaction of NiO support are relatively high.

NiO precursor to Ni: NiO the nickel catalyst precursor which directly or after reduction can lead to active nickel catalyst as

$NiO + H_2 - (\Delta) \rightarrow Ni$ $+$ H_2O
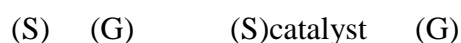
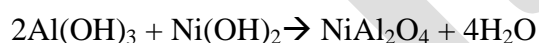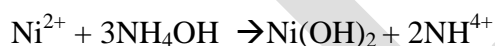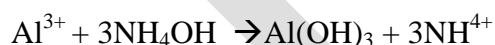(S)   (G)   (S)catalyst   (G)

This active nickel catalyst is used in the laboratory as well as in the industry as heterogenous catalyst for hydrogenation reaction. NiO has simple cubic crystal structure. In this Ni^{2+} and O^{2-} are alternately arranged.

Stoichiometric NiO: In this compound the number of cations& anions are exactly in the same ratio by the ideal chemical formula $Ni_{1.0}O_{1.0}$

Experimental:

1.   Preparation of NiAl$_2$O$_4$- the support:

Reaction:

$Al^{3+} + 3NH_4OH \rightarrow Al(OH)_3 + 3NH^{4+}$

$Ni^{2+} + 3NH_4OH \rightarrow Ni(OH)_2 + 2NH^{4+}$

$2Al(OH)_3 + Ni(OH)_2 \rightarrow NiAl_2O_4 + 4H_2O$

Procedure: The ammonium hydroxide method is used to prepare the spinal NiAl$_2$O$_4$ which is used as a support for nickel catalyst precursors.Appropriate amount of nickel and aluminium salts (NiSO$_4$/Ni (NO$_3$)$_2$/Al$_2$(SO$_4$)$_3$/Al(NO$_3$)$_3$) are weighted to make concentration of nickel and aluminium in 1:2 ratio. Dissolved in water and to this solution liquor ammonia is added till complete precipitation. The blue-green gelatinous precipitation of hydroxides of nickel and aluminium is obtained, which is filtered and dried.

2.   **Preparation of NiO(non-stichiometric) by nitrate of nickel**:

The simple calcination of Ni(NO$_3$)$_2$.6H$_2$O at 300^{0}C for 30 minutes yields non-stichiometricNiO.

$Ni(NO_3)_2.6H_2O$ -- $(300^0C)\rightarrow NiO + 2NO_2 + O_2 + 6H_2O$.
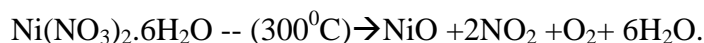
In preparation of NiO there is some controversy in stichiometric and non-stichiometric forms of NiO. So we have prepared both stichiometric and non-stichiometric forms of NiO.

### 3.   Preparation of NiO (stoichiometric) by carbonate

Reactons:

$NiSO_4.6H_2O + Na_2CO_3 \rightarrow NiCO_3 + Na_2SO_4$.

$NiCO_3 \rightarrow NiO$(stoichiometric, black) $+ CO_2$

Procedure: Nickel sulphate and Sodium carbonate gives nickel carbonate firstly, then after calcination of nickel carbonate gives nickel oxide (stoichiometric). The appropriate amount of compounds ($NiSO_4.6H_2O$, Na_2CO_3) is weighted accurately in 1:1 proportion. Then dissolve it in water, after dilution mix both the solution in each other. Then the precipitate of NiCO3 (bluish green) is filtered, wash and dried and calcinated to give stoichiometricNiO(black).

4.   Preparation of NiO(non-stichiometric) by Oxalate.

Reaction:

$NiSO_4.6H_2O + (NH_4)_2C_2O_4.H_2O \rightarrow NiC_2O_4$

$NiC_2O_4 \rightarrow NiO$ (non-stichiometric)
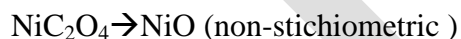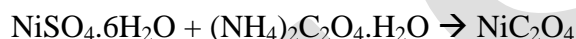
Procedure: from nickel sulphate and ammonium oxalate gives nickel oxalate fistly. Then after calcination of nickel oxalate gives nickel oxide (non-stichiometric) which is catalytically active Ni catalyst precursor. Appropriate amount of the compound (NiSO4.6H2O/ (NH4)2C2O4.H2O) is weighted accurately in 1:1 proportion. Then dissolved both the salts in minimum amount of water. Then heat both the solutions on a low flame up to 40^0C. Then mix both the solutions by constant stirring. The Ni-oxalate (bluish green) ppt, is formed is washed, filter and dried well to give Nio. This NiO is non-stichiometric which is act as bulk Ni-catalyst precursor.

Preparation of Impregnated Samples:

a)   Impregnation with Ni^{2+} nitrate over $NiAl_2O_4$(by SO_4^{2-})

Part I: Pore volume

The pore volume of support i.e. $NiAl_2O_4$ (by sulphate method) is found by measuring the volume of deionised water required to impregnate a known amount of sample until wetness. One gm. Of support is placed in a flask. A burette of 10ml is filled with distilled water. This water is added dropwise while the support is stirred with a sptula so that the powder is homogeneous as possible. No more water is added when the support is almost wet (it starts to stick to the spatula)

the volume of water is added can be seen by checking the level of the burette. This is the pre volume (ml/g) of the support. In other case, the pore, volume of the $NiAl_2O_4$ is 0.8ml/g .

Part II: Impregnation with nickel nitrate:

a green nickel nitrate hexahydrate solution is prepared by dissolving 6.5g $Ni(NO3)2.6H2O$ in 5ml distilled water. Taking into account the pore volume determined so that the final composition is 1.04g $Ni(NO3)2.6H2O/g$ support. This support is dried in an oven at 120^0C. After being calcinated at 350^0C, the sample is black.

b) Impregnation with Ni^{2+} nitrate over $NiAl_2O_4$(by nitrate)

Part I: Pore volume

The pore volume of support i.e. $NiAl_2O_4$ (by nitrate method) is found by measuring the volume of distilled water required to impregnate a known amount of sample until wetness. One gm. Of support is placed in a flask. A burette of 10ml is filled with distilled water. This water is added drop wise the powder is homogeneous as possible. No more water is added when the support is almost wet (it starts to stick to the spatula) the volume of water is added can be seen by checking the level of the burette. This is the pre volume (ml/g) of the support. In other case, the pore, volume of the $NiAl_2O_4$ is 0.8ml/g .

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Table1.Yield of samples:

Sr. no.	Name of samples	% yield	Colour& Appearance
1	$NiAl_2O_4$ by sulphate method	88.53%	Green, Crystalline
2	NiO by nitrate method (non-stichiometric)	88.40%	Gray, Amorphous
3	NiO by carbonate method (stoichiometric)	81.41%	Black, Amorphous
4	NiO by oxalate(non-stichiometric)	75.86 %	Green, Amorphous
5	Impregnated $NiAl_2O_4$ (by sulphate)	86.95%	Black, Amorphous
6	$NiAl_2O_4$ by nitrate method	89.86%	Green, Crystalline
7	Impregnated $NiAl_2O_4$ (by nitrate)	76.91%	Black, Crystalline

Method used for analysis:

Disintegration of samples:

Dilute the above prepared compound (NiO-bicarbonate) to prepare 7 ppm concentrated compound. Then adjust the PH to 4. Then 25 ml aliquot is taken for determination of total content of Ni^{2+} from this solution.

Titrimetric Estimation:

[Protocol-A]Principal: To determine the total aluminium and nickel contents in NiAl2O4 (by sulphate method) the complexometric titration method used. The EDTA is used as complexing reagent. Titrationg against Zn^{2+} solution. The amount of EDTA consumed = Amount of Ni^{2+} and Al^{3+} ion. From this difference % Ni^{2+} and % of Al^{3+} calculated.

Procedure: Pipet a 10ml aliquot of the disintegrated sample solution in a flask followed by adding 10ml of the bicarbonate-carbonate butter solution (pH=10) Transfer a 35ml of std. EDTA solution to the flask using a burette. Boil the mixture for 5min to speed up the formation of Al-EDTA complex. Add 5 drops of EBT indicator and mix it well. The solution is blue in colour. Back-titrate the solution with std. zinc solution until the colour changes to purple at end point.

[Protocol-B]Principal: To determine the nickel content in above solution the complexometric titration method used. The EDTA is used as a complexing reagent. Titrating against Zn^{2+} solution. The amount of EDTA consumed is equal to amount of Ni^{2+} from this difference % of Ni^{2+} is calculated.

Procedure: determination of Ni^{2+}: pipet out a 25 ml aliquot in a flask followed by adding 10ml PH butter(bicarbonate) transfer 25ml of standard EDTA solution. Back titrate the solution with Zn^{2+}. The End point is Blue to Wine red. The EBT is the indicator used.

Calculations:

Protocol- B Estimation of Ni^{2+} (NiO by <u>carbonate method</u>):

1ml1M EDTA=58.71mg of Ni.

As 74.709mg of NiO= 58.71 mg Ni.

25ml stock soilution = 2.2593 mg of Ni.

EDTA required for100ml   = 2.22593x100 /58.71   = 3.84ml.

 (Blank – Back) difference in the readings = 3.60ml

Amount of EDTA used by NiO Solution:

Observed reading (ml)	Expected reading (ml)	% of Ni observed
3.60	3.84	73.52

II) NiAl$_2$O$_4$(by sulphate method):

Protocol-A (Estimation of Ni^{2+}and Al^{3+}.

1ml1M EDTA=58.71mg of Ni + 53.96mg Al^{3+}.

Now, 1Ni Al$_2$O$_4$ = 1 Ni^{2+}+ 2Al^{3+}

As 76.67mg = (58.71+53.96) 112.67mg.

23.93mg = 15.2612 mg.

So 100ml stock solution = 15.2612 mg of Ni&Al.

25ml stock soilution = 3.8153 mg of Ni&Al.

EDTA required for100ml   = 3.8153x100/112.67   = 3.38ml.

values	Blank reading (ml)	Back reading (ml)	Difference (ml)
Expected	25.00	21.62	3.38
Observed	24.90	21.90	3.00

Protocol-B (Estimation of Ni^{2+})

1NiAl$_2$O$_4$= 1 Ni.

173.67 mg = 58.71 mg Ni.

23.93mg =7.9522 mg of Ni.

100ml stock solution = 7.9522 mg of Ni.

25ml stock solution = 1.9880 mg of Ni.

X = 1.9880x100/58.71   = 3.38ml.

 3.38ml EDTA solution = total Ni content (theoretical)

100ml solution = 58.71 mg Ni

3.00ml solution = 1.7613 mg Ni

100ml stock solution = 29.44 mg Ni

23.93ml $NiAl_2O_4$ = 7.0452 mg Ni

100ml stock $NiAl_2O_4$ = 29.44 mg Ni

i.e. % of Ni observed = 29.44 % mg.

values	Blank reading (ml)	Back reading (ml)	Difference (ml)	% of Ni
Expected	25.00	21.61	3.39	---
Observed	24.90	23.90	1.00	29.44

% of all can be back calculated from the difference between

Protocol-A & Protocol-B.

Protocol-A (Ni^{2+} + Al^{3+}) =3ml.

Protocol-B (Ni^{2+}) = 1ml.

The difference 3-1 = 2ml (Al^{3+}content)

Calculations:

Determination of Al^{3+}

$NiAl_2O_4$ = 2Al

176.67mg $NiAl_2O_4$= 53.96 mg.

23.93 mg = 0.2442mg Al^{3+}.

M = 0.009052M.

Amount of Al^{3+} in solution = ml of EDTA solution required.

0.009052 x 25 = 0.01 x V_2

V_2 = 22.63.

Blank reading = 25ml

Back reading = 25.00-22.63 = 2.37

100ml solution = 53.96mg Al^{3+}

2 ml solution = 1.5028 mg Al^{3+}

25 ml stock solution = 1.5028 mg Al^{3+}

100ml stock solution = 6.112 mg Al^{3+}

23.93mg $NiAl_2O_4$ = 6.0112 mg Al^{3+}

100 mg$NiAl_2O_4$ = 25.12 mg Al^{3+}

i.e. 25.12 mg of Al^{3+}

i.e. 25.012% Al^{3+} is present while expected % = 30.92 %.

Blank reading (ml)	Back reading (ml)	Difference (ml)	% of Al observed	% of Al expected
25.00	22.63	2.37	25.12	30.92

Estimation of $Ni^{2+}$and Al^{3+} from $NiAl_2O_4$(by sulphate method) using Protocol-A & Protocol-B methods:

Sr.no.	Method used	Difference between (blank-back)reading in ml	Metal in $NiAl_2O_4$ Solution	Amount of metal in %
1	Protocol-A	3.00	Ni + Al	60.36
2	Protocol-B	1.00	Ni	29.44
3	Protocol-(A-B)	2.00	Al	25.12

C) Estimation by AAS

Perkin – Elemer spectrophotometer is use for AAS study.

Wavelength = 2.32 nm.

Estimation of Nickel concentration using AAS has also been done. The repetition of this work is necessary because no satisfactory results were obtained.

The respective result for NiO (Prepared by carbonate method-stichiometrically) is given as follows:

% of Ni expected	% of Ni observed	% Error Observed
78.58	75.68	10.00

Result and Discussion:

Titrimetric analysis:

Sr. no.	Name of sample	Metal	% observed
1	**Protocol- B Estimation of Ni^{2+} (NiO by carbonate method)**	Ni^{2+}	73.52
2	**Estimation of Ni^{2+}and Al^{3+} from NiAl$_2$O$_4$(by sulphate method) using Protocol-A & Protocol-B methods**	Ni^{2+} Al^{3+} Ni^{2+}+ Al^{3+}	29.44 30.92 60.36
3	**Estimation by AAS Ni^{2+} fromNiO (Prepared by carbonate method-stichiometrically)**	Ni^{2+}	75.68

Conclusion:

In synthesis of bulk and supported nickel catalyst precursors are NiAl$_2$O$_4$ by sulphate method, NiO by nitrate method (non-stichiometric), NiO by carbonate method (stoichiometric), NiO by oxalate(non-stichiometric) , Impregnated NiAl$_2$O$_4$ (by sulphate), NiAl$_2$O$_4$ by nitrate method, Impregnated NiAl$_2$O$_4$ (by nitrate).

NiO –NiAl$_2$O$_4$ can be expected to give greater degree of reduction & greater reducibility than catalyst NiO-r-Al$_2$O$_3$and therefore, expected to be better precursor.

AAS Analysis of Ni^{2+} in NiO is by carbonate method is nearly 10%, For all other samples the error in percentage nickel is greater than 10%.

Acknowledgement:

References:

1. F.Medina,T.B.Suriras, Y.Cesteros and P.SalagreI.Chem. Educ.2002.79.489.
2. Walter de GruyterBerline, New york 1994. Concise Encyclopedia chemistry.
3. S.K.Mookerjee, Oxford university press, concise dictionary of chemistry.
4. D.F.Shriver, P.W.Stkins, Oxford University press,, 3rd edition Inorganic chemistry.
5. A textbook of Quantitative inorganic analysis including elementary instrumental analysis 3rd edition,1973,Aa.i.vogel
6. Langes hand book of chemistry Mc Grottill 13th edition. 1987.
7. Alessandro, Trovarelli, Catalysis by veria and related materials http/www.Google.Scholar.com (Assey March 2007.

8. Sandra E DannLoughborough university reactions and characterization of solids. The Royal Society of chemistry 2000.

9. V Zuzaniuk, R Prins; Journal of CatalysisVolume 219, Issue 1, 1 October 2003, Pages 85–96

10. QingxinGuan,Wei Li, ,MinghuiZhang,KeyiTao;Journal   of   CatalysisVolume   263, Issue 1, 1 April 2009, Pages1-3.