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Optimization of process parameters for synthesis of silica–Ni nanocomposite by design of experiment

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Abstract. **The optimum combination of experimental variable, temperature, time of heat treatment under nitrogen atmosphere and amount of Ni-salt was delineated to find out the maximum yield of nanophase Ni in the silica gel matrix. The size of Ni in the silica gel was found to be 34 and 45 nm for the two chosen compositions, respectively. A statistically adequate regression equation, within 95% confidence limit was developed by carrying out a set of active experiments within the framework of design of experiment. The regression equation is found to indicate the beneficial role of temperature and time of heat treatment.**

Keywords. **Sol–gel; Ni; design of experiments; nanocomposites.**

1. Introduction

The synthesis and characterization of nanostructured materials has found importance world over, because of their novel properties and potential for applications in many fields. Good reviews on basic understanding are available (Gorla *et al* 1999; Gao and Bando 2002; Aldal *et al* 2005). Many methods have been used for synthesis of nanomaterials of which sol–gel technique is very versatile (Das *et al* 1990; Rao 1993; Mallick *et al* 2006). This technique has been exploited to synthesize metal–insulator nanocomposites. Insulator nanocomposites have possible applications in optical switches and single electron transistor (Yeshchenko *et al* 2008), fine soft magnetic materials (Tang *et al* 2004), microwave absorbing and shielding materials (Peng *et al* 2008), super paramagnet (Fonseca 2003), etc. The kinetics of reduction of the metal salts in silica gel matrix is widely studied. Detailed kinetic analysis for *in situ* reduction of transition metal salts in silica is reported (Basumallick *et al* 1999) and for understanding the mechanism of reduction and computation of the activation energy for silica–alumina gel matrix is also available (Mallick *et al* 2006). The amount of metal along with other morphological characterization influences the property (Granquivst and Hunderi 1977). However, very little work has been done on the quantitative relationship between the reduction of metal salts in silica powder as a function of experimental parameters, viz. temperature and time of reduction (Roy *et al* 2007). It was, therefore, thought to be worthwhile to find out such a quantitative relationship and this paper deals with the development of statistically adequate relationship within the framework of design of experiment.

2. Experimental

The temperature of reduction (Z_1), time of reduction (Z_2), amount of nickel chloride (Z_3) were taken as the independent process parameters. As per the requirement of design of experiment, each parameter must have upper and lower levels. Table 1 summarizes the upper and lower levels chosen for this experiment. Thus, it required to make 2^3 samples along with three replicates at the base level. First, a set of four gel samples were made. Each one with TEOS:H_2O:C_2H_5OH ratio of 1:1:2 by volume, respectively was prepared. A homogeneous solution was prepared with 1 mL of distilled water, containing 0·159 g of $NiCl_2$ along with 50% excess glucose over stoichiometric requirement of complete reduction of $NiCl_2$, 5 mL of ethyl alcohol and 4 mL of distilled water. The solution was stirred thoroughly for getting a homogeneous solution. A second homogeneous solution of 5 ml C_2H_5OH and 5 ml tetraethyl orthosilicate (TEOS) was also prepared under constant magnetic stirring. The first solution was added dropwise to the second one under continuous stirring with a magnetic stirrer. The resulting solution was left for gelling at room temperature.

A second set of four gel samples were made similarly, with the same ratio of TEOS:H_2O:C_2H_5OH as mentioned earlier, but it contained double the amount of $NiCl_2$ compared to that of the first set.

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Table 1. Upper and lower levels of process parameters.

Parameter	Upper level	Lower level
Z_1	900 °C	700 °C
Z_2	8 min	1 min
Z_3	0·318 g	0·159 g

A set of three gel samples for base level was made exactly the same way, with the same ratio of TEOS:H_2O:C_2H_5OH, but each gel containing 0·2385 g of $NiCl_2$.

The eight samples were then heat treated as per the temperature and time given in table 1, in a tubular electrically heated furnace under constant flow of dry oxygen free nitrogen.

The reaction produced HCl vapour which was swept away from the reaction site and was bubbled through the gas absorbing towers containing double-distilled water, where HCl vapour was absorbed. pH of the resultant solution was measured from which the fraction of $NiCl_2$ reduced was calculated and is summarized in table 2. Table 2 also contains data of three replicates each heat treated in N_2 atmosphere at the base level of 800°C for a period of 4 1/2 min.

Two typical heat treated samples were ground and passed through 400 mesh and XRD patterns of these were taken using CuKα monochromatic radiation in Regaku make Ultima III, XRD instrument.

3. Results and discussions

This section basically involves two parts. The first part deals with the reduction of $NiCl_2$ in the nanopores of silica gel to metallic Ni and its identification while the second part deals with the statistical analysis of the reduction data.

In situ reduction of $NiCl_2$ in silica gel occurs as follows as reported elsewhere in detail

$$C_6H_{12}O_6 = 6C + 6H_2O\uparrow,$$

$$C + H_2O = CO\uparrow + H_2\uparrow,$$

$$H_2 + NiCl_2 = Ni + 2HCl\uparrow .$$

The nanoporous silica gel matrix plays a very important role in this *in situ* reduction. The first one is that the nanopores restrict the reduced metal to be in the nanometric dimension. Secondly, it is important to note that the reactions occur in nanopores simultaneously throughout the bulk of silica gel matrix, which make kinetics of reduction much faster. Thirdly, since the nanosized metal is entrapped in the silica matrix subsequently there is hardly any oxidation.

Figures 1 and 2 represent XRD patterns of the gel samples containing 5 and 10 wt% $NiCl_2$, respectively which were heat treated at 900 °C for 8 min. Computed '*d*' values are in good agreement with standard '*d*' values of metallic Ni. Peaks corresponding to metallic Ni are indicated in both the figures.

Table 2. Fraction of $NiCl_2$ reduced for different combinations of experimental variables.

Z_1 (in °C)	Z_2 (in Min)	Z_3 (in gM)	Fraction $NiCl_2$ reduced
900	8	0·318	0·980
900	1	0·318	0·063
900	8	0·159	0·982
900	1	0·159	0·066
700	8	0·318	0·577
700	1	0·318	0·013
700	8	0·159	0·634
700	1	0·159	0·021
800	4·5	0·238	0·620
800	4·5	0·238	0·680
800	4·5	0·238	0·700

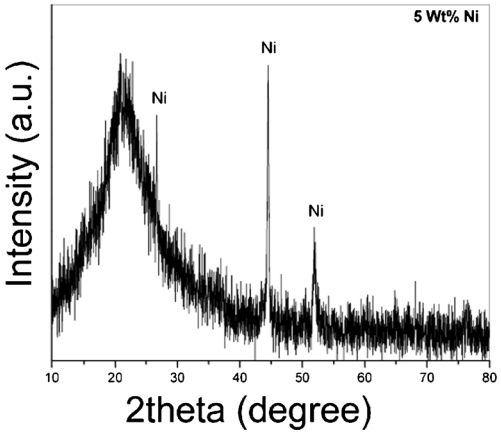

Figure 1. XRD pattern of sample containing 5 wt% Ni heat treated at 900 °C for 8 min in nitrogen atmosphere.

The value of sin θ/λ in each of samples (figures 1 and 2) for the hump is 0·116, very close to 0·12, which is attributed to amorphous silica (Warren and Biscal 1938). This is plausibly due to slow kinetics of crystallization of amorphous silica arising out of lower reduction temperature for a shorter period of time.

Scherrer formula (Cullity 1978) given below was used to compute the particle size of nickel

$$t = 0{\cdot}9\lambda/B\cos\theta,$$

where t is the average particle size in Å, B the width of the peak at half-maximum in radian and λ the wavelength of X-ray in Å.

The highest intensity peak in each case was used to compute the size of Ni which were 34 nm for 5 wt% Ni–SiO_2 composite and 46 for 10 wt% Ni–SiO_2 composite, respectively.

Figure 3 shows clearly nanometric dimension of the nickel particles. From the inset observed, $d = 0{\cdot}21$ nm matches reasonably well with the reported value of $d = 0{\cdot}203$ nm of the metallic Ni.

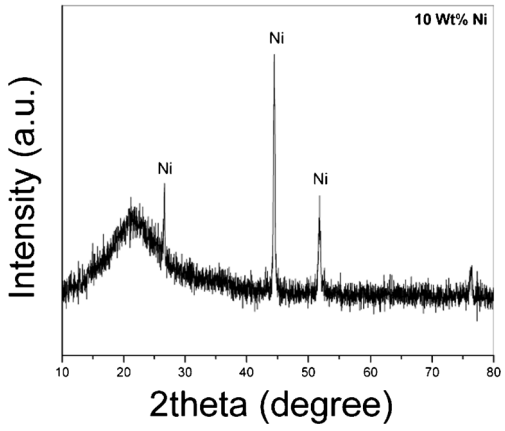

Figure 2. XRD pattern of sample containing 10 wt% Ni heat treated at 900 °C for 8 min in nitrogen atmosphere.

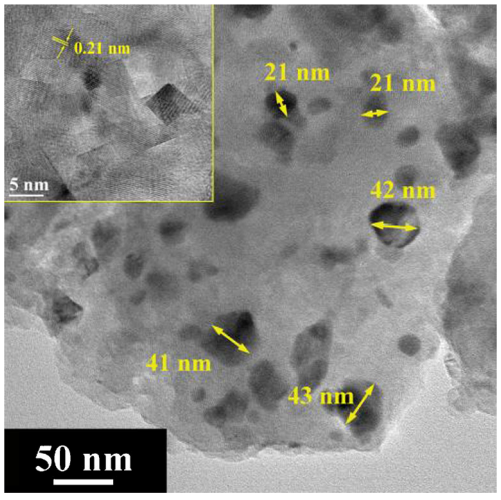

Figure 3. TEM image of sample containing 5 wt% Ni heat treated at 900 °C for 8 min in nitrogen atmosphere and lattice image is included in inset.

Table 2 contains experimentally determined fraction of $NiCl_2$ reduced for different combinations of experimental conditions along with three replicates at the base level.

Statistical analysis on reduction data was based within the framework of design of experiment:

Experimental variables Z_j, $j = 1, 2, 3$ on natural scale, respectively representing temperature, time and weight of $NiCl_2$ were converted to dimension less variables x_j, $j = 1, 2, 3$ such that $x_j = +1, -1$ and 0, respectively representing the upper level, lower level and base level (Kafarov 1976), respectively. Tables 1 and 2 are used to construct the coded design matrix in terms of x_j and are given in table 3.

The response function y is given by the following linear regression equation,

$$y = a_0x_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_{12}x_1x_2 + a_{13}x_1x_3 + a_{23}x_2x_3 + a_{123}x_1x_2x_3, \quad (1)$$

Table 3. Coded design matrix.

Factors on dimensionless scale			Dummy variables	Fraction $NiCl_2$ reduced
x_1	x_2	x_3	x_0	y
+1	+1	+1	+1	0·980
+1	−1	+1	+1	0·063
+1	+1	−1	+1	0·982
+1	−1	−1	+1	0·066
−1	+1	+1	+1	0·577
−1	−1	+1	+1	0·013
−1	+1	−1	+1	0·634
−1	−1	−1	+1	0·021

where

$$a_j, \text{ for } j = 0, 1, \ldots .3, \quad (2)$$

$$a_{ij}, \text{ for } i = 1, 2, \; j = i + 1, \ldots . .3. \quad (3)$$

The equations contain first order, second order interaction coefficients, respectively and a_{123} is the third order interaction coefficient.

Using the data of table 3, interaction coefficients are evaluated by Kafarov (1976),

$$a_j = 1/N \sum_{l=1}^{N} x_{lj}y \quad \text{for } j = 1, \ldots 3, \quad (4)$$

$$a_{ij} = 1/N \sum_{l=1}^{N} x_{il}x_{jl}y \quad \text{for } i = 1, 2, \; j = i + 1, \ldots 3, \quad (5)$$

$$a_{ijk} = 1/N \sum_{l=1}^{N} x_{il}x_{jl}x_{kl}y \quad \text{for } i = 1, \; j = i + 1, \; k = i + 2, \quad (6)$$

N is the total number of experiments. In this case N is equal to 8. In order to find out significant coefficients, following student t test was carried out.

$$t_j = \frac{|a_j|}{S_{aj}}, \quad (7)$$

where $a_{j's}$ are interaction coefficients calculated by (4–6). S_{aj}, the estimated variance of coefficients are given by:

$$S_{aj} = S_e/\sqrt{N}, \quad (8)$$

where S_e, the square root of error mean square given by

$$S_e^2 = \frac{1}{2}\left[\sum_{i=1}^{3}\left\{y_i^0 - \left(\sum_{l=1}^{3} y_l^0/3\right)\right\}^2\right], \quad (9)$$

y_i^0 is the yield of nickel at the base level for ith replicate. Using the data of replicates at the base level (table 2),

the computed S_e turns out to be 0·0416. Thus, using (7) along with (8) and (9), the 't' values were calculated and is tabulated below:

$$t_0 = 28{\cdot}36 \quad t_{12} = 5{\cdot}57,$$
$$t_1 = 7{\cdot}19 \quad t_{13} = 0{\cdot}51,$$
$$t_2 = 25{\cdot}59 \quad t_{23} = 0{\cdot}40,$$
$$t_3 = 0{\cdot}59 \quad t_{123} = 0{\cdot}42.$$

The tabulated value of student t distribution, $t_p(f)$ is 4·3 for a significance value of $P = 0{\cdot}05$ and degree of freedom $f = 2$. Comparing the computed t-values with 4·3, it was found that t_{13}, t_{23}, t_3 and t_{123} values were less and hence, the corresponding coefficients are statistically insignificant in the regression equation (1). Thus regression equation containing only the significant interaction coefficients is given by:

$$y = 0{\cdot}417 + 0{\cdot}10575x_1 + 0{\cdot}37625x_2 + 0{\cdot}082x_1x_2, \quad (10)$$

whether (10) is statistically adequate was tested by Fisher's variance ratio (F) test which is given by

$$F = S_r^2/S_e^2, \quad (11)$$

where S_e^2 is the error mean square and has already been evaluated by (9).

S_r^2 is the residual mean square and is given by:

$$S_r^2 = \left\{\sum_{i=1}^{N}\left(\hat{y}_i - y_i\right)^2\right\} / (N-1), \quad (12)$$

$\hat{y}_i$ and y_i are the yield of nickel computed theoretically by (10) and experimentally obtained for ith experiment, respectively. l stands for the number of significant coefficient. The value of l as obtained from student t test is 4. Using table 3, (10) and (12), the ratio F computed by (11) is 0·24. For significance level of $p = 0{\cdot}05$, and for degrees of freedom $f_1 = N–l = 8-4 = 4$ and $f_2 = 2$, the tabulated value of $F_{0{\cdot}05}(4,2)$ is 19·3 (Grewall 1998).

Since, $F < F_{0{\cdot}05}(4,2)$, the estimated regression equation is statistically adequate. To test the validity of (10) independently a point $x_1 = 0{\cdot}5$, $x_2 = 0{\cdot}5$ was taken in the design space. The experiment was replicated thrice and the experimental fraction conversions were 0·82, 0·87 and 0·77, respectively. Based on these data, the calculated $F(4, 2) = 0{\cdot}18$ which is less than the theoretical $F_{0{\cdot}05} = 19{\cdot}3$. This shows that the predicted value by the regression equation is within 95% confidence limit.

The statistically adequate regression (10) is linear. It is, therefore, expected that the maximum fraction reduction of $NiCl_2$ occurs at the design boundary. From (10), the maximum predicted yield of Ni is found to be 0·981 for $x_1 = 1$ and $x_2 = 1$, which is in excellent agreement with the experimentally observed yield of 0·982 for $x_1 = 1$ and $x_2 = 1$ (table 3). This means that maximum reduction occurs when the sample is heat treated at the highest temperature of 900 °C for longest time of 8 min for this particular design space under consideration and this is what is expected from the kinetic point of view.

4. Conclusions

(I) A statistically adequate regression equation as a function of reduction temperature and time is developed by the design of experiment.
(II) With the increase of reduction temperature and time the yield of metallic Ni increases.
(III) The maximum yield of nickel is obtained at the maximum temperature of reduction of 900 °C and the time of 8 min.

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