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Statistical Optimization of process parameters for SiO_2-Nickel nanocomposites by in-situ reduction

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Abstract
The optimum combination of process parameters - temperature, time of reduction under nitrogen atmosphere and amount of $NiCl_2$ was delineated to find the maximum yield of nanocrystallite Ni in the synthesized silica gel matrix. A statistically adequate regression equation, within 95% confidence limit was developed by carrying out a set of experiments within the framework of design of experiment. The regression equation is found to indicate the beneficial role of the temperature and time of reduction.
Keywords: Sol-gel, Ni, Design of experiments, Nanocrystallite

I. Introduction

The kinetics of the reduction of the metal salts in silica gel matrix has been widely studied. Detailed kinetic analysis have been carried out ,for in situ reduction of transition metal salts in silica [1] and silica- alumina gel matrix [2] to understand the mechanism of reduction and to compute the activation energy. This would help to control and tailor make the nanocomposites. The amount of metal along with other morphological characterization would influence the properties [3]. However, hardly any work has been done on the quantitative relationship between the reduction of metal salts in silica powder as a function of experimental parameters- temperature, time[4]. It would therefore be worthwhile to find such a quantitative relationship and in this research work we report the development of statistically adequate relationship within the frame work of design of experiment.

The properties of the Nanocomposites are structure dependent. By structure we mean atomic arrangement, shape , size , its distribution and the amount of phase(s). By changing a single or a combination of variables one can design and generate novel properties. Even Nanocomposites processing identical composition often shows significant deviation from their properties if their processing conditions are changed. Hence it may be concluded that, as nanostructured materials are in a non-equilibrium state of condensed matte, their properties are not only functions of chemical composition, shape, size and amount, they are also strongly dependent on the mode of preparation and their thermal history. [5].

II. Experimental procedure

Design of Experiment for Synthesized silica-5wt% & 10wt% Nickel samples

The temperature of reduction(Z_1), time of reduction(Z_2) , Nickel chloride(Z_3) are taken as the independent process parameters. As per the requirement of design experiment, each parameter must have a upper and lower level. Table 1 summarizes the upper and lower levels chosen for this experiment. Thus it requires to make 2^3 samples along with three replicates at the base level.

.First a set of four gel samples were made following the same procedure as mentioned earlier. 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.

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 0.2385gm of $NiCl_2$.

The eight samples were then heat treated as per the temperature and time given in table 1. Reductions of Silica –Nickel Nanocomposites were carried out in a programmable electrically heated furnace with a PID controller under nitrogen atmosphere and heating rate was 6^oC /min. The reaction produced HCl vapour is swept away from the reaction site by the flow of N_2 gas and is bubbled through the gas absorbing towers containing distilled water where HCl vapour is absorbed. The pH of the resultant solution is measured from which the fraction of $NiCl_2$ reduced is calculated and is summarized in Table 2. Table 2 also contains the data of three replicates (necessary for statistical t-test) each heat treated in N_2 atmosphere at the base level of 400^oC for a period of 7½ minutes of samples.

III. Results and Discussion:

The insitu reduction of $NiCl_2$ in silica gel occurs as follows as reported elsewhere in details [5]

$C_6H_{12}O_6 = 6C + 6H_2O \uparrow$
$C + H_2O = CO\uparrow + H_2\uparrow$
$H_2 + NiCl_2 = Ni + 2HCl\uparrow$.

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.

Table 1: The upper and lower level of Process parameters

Parameter	Upper level	lower level
Z_1	550^{o}C	350^{o}C
Z_2	12 minutes	3 minutes
Z_3	0.318gm	0.159gm

Table 2 contains the experimentally determined fraction $NiCl_2$ reduced for different combination of experimental conditions along with the three replicates at the base level[6]

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

Z_1 (in ^{o}C)	Z_2 (in Minutes)	Z_3 (in gm)	Fraction $NiCl_2$ reduced
550	12	0.318	0.9803
550	3	0.318	0.3559
550	12	0.159	0.9940
550	3	0.159	0.5039
350	12	0.318	0.2893
350	3	0.318	0.1003
350	12	0.159	0.3736
350	3	0.159	0.1388
450	7.5	0.238	0.6113
450	7.5	0.238	0.6859
450	7.5	0.238	0.6400

Statistical Analysis based on reduction data within the frame work of design of experiment:

Experimental variables Z_j , j =1,2,3 on natural scale respectively representing temperature, time and weight of $NiCl_2$ are converted to dimension less variables x_j , j = 1,2,3 such that x_j = +1, -1 and 0 respectively represent the upper level, lower level and base leve[6] respectively. Tables 1, 2and 3 are used to construct the coded design matrix in terms of x_j and is given in table 3.

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

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

Where,

a_j, *for* $j = 0, 1,\ldots.3$ (2)

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

represent the first order , second order interaction co-efficients respectively and a_{123} is the third order interaction co-efficient.

Table 3: Coded design matrix

Factors on dimension less scale			Dummy variables	Fraction $Nicl_2$ reduced
x_1	x_2	x_3	x_o	y
+1	+1	+1	+1	0.9803
+1	-1	+1	+1	0.3559
+1	+1	-1	+1	0.9940
+1	-1	-1	+1	0.5039
-1	+1	+1	+1	0.2893
-1	-1	+1	+1	0.1003
-1	+1	-1	+1	0.3736
-1	-1	-1	+1	0.1388

Using the data of table 3 and the following equations given by(4,5,6), the interaction co-efficients are evaluated

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

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

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

Where N is the total number of experiments. In this case N equals to 8. . In order to find out the significant co-efficients, following student t test is carried out as follows.

$$t_j = \frac{|a_j|}{S_{aj}} \tag{7}$$

Where $a_{j's}$ are interaction co-efficients calculated by eqs (4-6). The S_{aj} , the estimated variance of co-efficients is given by

$$S_{aj} = S_e / \sqrt{N} \tag{8}$$

Where S_e, the square root of error mean square is given by

$$S_e^2 = 1/2[\sum_{i=1}^{3}\{y_i^0 - (\sum_{l=1}^{3} y_l^0/3)\}^2] \tag{9}$$

y_i^0 is the yield of Nickel at the base level for i^{th} replicate. Using the data of the replicates at the base level(ref. table2) the computed S_e turns out to be 0.0375. Thus using Eq (7) along with eqs (8), and (9) , the t values are calculated and tabulated below

$t_o = 35.92$	$t_{12} = 6.638$
$t_1 = 18.57$	$t_{13} = 0.374$
$t_2 = 14.78$	$t_{23} = 0.85$
$t_3 = 2.73$	$t_{123} = 1.73$

The tabulated value of student t distribution, $t_p(f)$ is 4.3 for a significance value of P= 0.05 and degree of freedom f=2. Comparing the computed t-values with 4.3, it is found that t_{13}, t_{23}, t_3 and t_{123} values are less and hence the corresponding co-efficients are statistically insignificant in the regression equation (1).
Thus regression equation containing only the significant interaction co-efficients is given by

$$y = 0.467 + 0.2415x_1 + 0.1922x_2 + 0.0863x_1x_2 \tag{10}$$

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

$$F = S_r^2 / S_e^2 \tag{11}$$

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

S_r^2 the residual mean square and is given by

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

$\hat{y}_i$ and y_i are the yield of nickel theoretically computed by Eq.(10) and experimentally obtained for the i^{th} experiment respectively and l stands for the number of significant co-efficients.. The value of l as obtained from student t test is 4. Using table 3, Eqs.(10)&(12), the ratio F computed by eq(11) is 2.71. For significance level of p=0.05,and for degrees of freedom $f_1 = N-l$=8-4= 4 and f_2 =2, the tabulated value of $F_{0.05}$ (4,2) is 19.3 [7] Since the $F<F_{0.05}(4,2)$,the estimated regression equation is statistically adequate.
The statistically adequate regression equation(10) is linear. It is therefore expected that the maximum fraction reduction of $NiCl_2$ would occur at the design boundary. From equation (10) the maximum predicted yield of Ni is found to be 0.987 for x_1=1 and x_2=1, which is in excellent agreement with the experimentally observed yield of 0.994 for x_1=1 and x_2=1(ref table 2). This means that maximum reduction occurs when the sample is heat treated at the highest temperature 550^{o}C for longest time of 12 minutes for this particular design space under consider and this is what is expected from the kinetic point of view.

IV. Conclusions

1. A statistically adequate regression equation can be used to successfully predict the yield of reduction of $NiCl_2$ in the silica matrix as a function of reduction temperature and time has been developed by the design of experiment.
2. The effect of temperature is most predominant factor.

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