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OPTIMIZATION OF PREPARATION FOR MAGNESIUM OXIDE BY CALCINATION FROM BASIC MAGNESIUM CARBONATE USING RESPONSE SURFACE METHODOLOGY

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Abstract

The conditions of technique to prepare magnesium oxide by calcination from basic magnesium carbonate were optimized using a central composite design (CCD) of response surface methodology (RSM). Two quadratic equation models for decomposition rate and activity of magnesium oxide were built and effects of main factors and their corresponding relationships were obtained. The statistical analysis of the results showed that in the range studied the decomposition rate and activity of magnesium oxide were significantly affected by the calcination temperature and calcination time. The optimized calcination conditions were as follows: the calcination temperature 666.99℃ and the calcination time 2.12 h, respectively. Under these conditions the decomposition rate of basic magnesium carbonate was 92.1971%, and the activity of magnesium oxide was 155.503 mg I_2/g MgO. The validity of the model was confirmed experimentally and the results were satisfactory. In addition, the sample was characterized by X-ray Diffraction (XRD).

Introduction

Magnesium oxide has received a great deal of attention for its applications in the chemical and electronic industries. MgO powder has been utilized as a catalyst and catalyst support [1-4], a fundamental material for chemical heat pump and it is very appropriate for insulation applications due to their low heat capacity and high melting point [5]. The most conventional method of synthesis of MgO is the decomposition of various magnesium salts or magnesium hydroxide.

Generally, the traditional approach "one variable at a time (OVAT)" is used to analyze the thermal decomposition process of basic magnesium carbonate. In OVAT, the effect of each experimental factor is investigated by altering the level of one factor at a time while maintaining the level of the other factors constant. Furthermore, this technique is not only time and work demanding, but completely lacks in representing the effect of interaction between different factors [6]. In order to solve these problems, it is necessary to find a multivariate statistic technique for optimization of preparation processes. Response surface methodology (RSM) might be a useful method to optimize preparation processes. RSM is a collection of mathematical and statistical techniques useful for analyzing the effects of several independent variables. The main advantage of RSM is the reduced number of experimental trials needed to evaluate multiple parameters and their interactions [7]. It can deal with multivariate experimental design strategy, statistical modeling and process optimization [8]. Several previous researchers have proved that RSM was a powerful statistical tool in process optimization, and it has just recently been applied to optimize the process parameters for biosorption of metals [9] or dyes [10] from synthetic solutions. However, as far as known to the authors, there have been very few studies to optimize the preparation of magnesium oxide from basic magnesium carbonate by the RSM approach. The aim of this work was to optimize the thermal decomposition process of basic magnesium carbonate parameters with a consideration of response by applying RSM. A quadratic model was derived to describe the effects of calcination temperature and calcination time on the decomposition rate of basic magnesium carbonate and activity of magnesium oxide. The crystal structure of magnesium oxide under the optimum condition was also analyzed.

Experimental

Calcination Experiments

The calcination experiments were carried out at the different calcination temperatures and calcination times of sample. Initially, the Muffle furnace was preheated with a speed of 10 ℃·min^{-1} until the desired temperature was reached. Then the basic magnesium carbonate was weighed and placed inside the ceramic crucible which was located in the center of the conventional Muffle furnace. During the reaction, the temperature was monitored by a temperature controller system, namely the PID (proportional integral derivative). Several cycles of experiment were repeated. For each cycle, a reaction was performed for a fixed duration, once the fixed duration is over, the experiment was stopped immediately. The product was moved out from the Muffle furnace and put into the drier rapidly. They were naturally cooled to the room temperature. The final weight (m) of sample was weighted subsequently, from which the decomposition rate was calculated based on the following equation:

$$Y = \frac{m_0 - m}{m_0 \times w_t} \times 100\% \quad (1)$$

where M and M_0 are final weight and initial weight of sample, respectively; W_t means theory value of weight loss, which is the total weight loss of basic magnesium carbonate during the thermal decomposition; Y is decomposition rate of basic magnesium carbonate.
Iodimetric titration was used to analyze the activity of magnesium oxide.

Designing Experiment Using Response Surface Methodology

RSM was employed to optimize the calcination conditions in order to obtain a qualified magnesium oxide, and CCD was employed to design the experiments. This method helps to optimize the effective parameters with a minimum number of experiments and also analyze the interaction between the parameters and results [11]. Based on our previous work, the effects of two independent variables, x_a (calcination temperature), and x_b (calcination time), at five level were investigated using

central composite design. The rank of values associated with the variables: calcination temperature (℃) was 600 and 700, and calcination time (h) ranged between 1.5 and 2.5 (Table 1). Generally, a second-order polynomial model with main, quadratic and interaction terms can be developed to fit the experimental data obtained from the experimental runs conducted on the basis of CCD. The experimental data obtained from the designed experiment were analyzed by the response surface regression procedure using the following second-order polynomial equation:

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i \chi_i + \sum_{i=1}^{n} \beta_{ii} \chi_i^2 + \sum_{i<j} \beta_{ij} \chi_i \chi_j \qquad (2)$$

where Y is the predicated response, β_0 is a constant, β_i is the ith linear coefficient, β_{ii} is the ith quadratic coefficient, β_{ij} is ijth interaction coefficient, x_i, x_j are the coded values of independent variables, and the terms $x_i x_j$ and x_i^2 represent the interaction and quadratic terms, respectively.

Table 1 Independent variables and their levels for central composite rotatable design

Variables	Symbol	Range and levels				
		-1.41421	-1	0	1	1.41421
calcination temperature /℃	x_a	579.25	600	650	700	720.71
calcination time / h	x_b	1.29	1.5	2	2.5	2.71

XRD Analysis

The X-ray diffraction analysis of the final solid product under optimization conditions were carried out using D/max-2200 Diffractometer (Japan) with Ni-filtered CuKa radiation under air atmospheres. The identification of the completeness of the magnesium oxide was made by comparing the diffraction peaks of each compound in the sample with the ones of the standard magnesium oxide. If the diffraction pattern of the final solid product satisfactorily matched with that of the standard magnesium oxide, it means that the decomposition of basic magnesium carbonate is complete.

Results and Discussion

Data Analysis and Evaluation of the Model by RSM

The experiments were conducted based on the design matrix under the defined conditions and the responses obtained from the experimental runs are shown in Table 2.

Table 2 shows the total number of 13 experiments as per CCD method. The experimental sequence was randomized in order to minimize the effects of the uncontrolled factors. Five experiments were repeated in order to estimate the experimental error. According to the sequential model, the sum of squares can be obtained, and the models were selected based on the highest order polynomial where the additional terms were significant and the models were not aliased. The responses of decomposition rate and activity of magnesium oxide were considered in studying the effect of process variables. The responses of decomposition rate and activity of magnesium oxide and the independent variables were used to develop two empirical models, which are presented by Eq. (3) and Eq. (4):

Table 2 Experimental design matrix and results

Run	Calcination variables		Decomposition rate of basic magnesium carbonate, Y_1 / %	Activity of magnesium oxide, Y_2 / mg/g MgO
	Calcination temperature, x_a / ℃	Calcination time, x_b / h		
1	600(-1)	1.5(-1)	85.41	136
2	700(+1)	1.5(-1)	92.68	137
3	600(-1)	2.5(+1)	87.20	134
4	700(+1)	2.5(+1)	93.15	135
5	579.29(-1.41421)	2.0(0)	83.58	124
6	720.71(+1.41421)	2.0(0)	93.91	127
7	650(0)	1.29(-1.41421)	87.41	142
8	650(0)	2.71(+1.41421)	92.33	146
9	650(0)	2.0(0)	90.15	158
10	650(0)	2.0(0)	91.71	157
11	650(0)	2.0(0)	90.71	156
12	650(0)	2.0(0)	91.03	159
13	650(0)	2.0(0)	90.91	157

$$Y = 90.90 + 3.48\chi_a + 1.15\chi_b - 0.33\chi_a\chi_b - 1.00\chi_a^2 - 0.44\chi_b^2 \qquad (3)$$

$$Y = 157.40 + 0.78\chi_a + 0.21\chi_b - 15.76\chi_a^2 - 6.51\chi_b^2 \qquad (4)$$

The quality of the two models developed was evaluated based on the correlation coefficient value (Table 3 and Table 4). The R^2 value for Eq. (3) was 0.9629 and for Eq. (4) was 0.9902 which indicated that 96.29% variability of the total variation in the decomposition rate was attributed to the experimental variables studied and 99.02% variability of the total variation in the activity of magnesium oxide was attributed to the experimental variables studied. The closer the R^2 value to unity, the better the model will be as it will give predicted values which are closer to the actual values for the response. The R^2 of 0.9629 for Eq. (3) was considered relatively high, indicating that there was a good agreement between the experimental decomposition rate and the predicted one from this model. The R^2 of 0.9902 for Eq. (4) was considered relatively high, indicating that there was a good agreement between the experimental activity of magnesium oxide and the predicted one from this model.

Furthermore, analysis of variance (ANOVA, also a part of RSM) was further carried out to justify the adequacy of the model. The ANOVA for the quadratic model for decomposition rate and activity of magnesium oxide are presented in Table 3 and Table 4. The model's adequacy was tested through the lack of fit F-test, in

which the residual error was compared to the pure error. According to the software analysis, "Lack of fit F-values" of 3.34 and 3.44 imply that the lack of fit was not significant relative to the pure error due to noise. The "Model F-values" of 36.31 and 140.99 imply that the two models were significant. Value of "Prob > F" less than 0.05 indicates that the two models terms are significant [12], whereas the values greater than 0.1000 are not significant.

Table 3 Analysis of variance (ANOVA) for response surface quadratic model for the decomposition rate of basic magnesium carbonate

Source	Sum of squares	D_f	Mean square	F-value	Prob>F
Model	115.54	5	23.11	36.31	<0.0001
Residual	4.45	7	0.64		
Lack of fit	3.18	3	1.06	3.34	0.1374
Pure error	1.27	4	0.32		
Cor total	119.99	12			

R^2=0.9629; R^2adj=0.9364; adequate precision=18.155(>4)

Table 4 Analysis of variance (ANOVA) for response surface quadratic model for the activity of magnesium oxide

Source	Sum of squares	D_f	Mean square	F-value	Prob>F
Model	1874.16	5	374.83	140.99	<0.0001
Residual	18.61	7	2.66		
Lack of fit	13.41	3	4.47	3.44	0.1319
Pure error	5.20	4	1.30		
Cor total	1892.77	12			

R^2=0.9902; R^2adj=0.9831; adequate precision=29.455(>4)

Response Surface Analysis

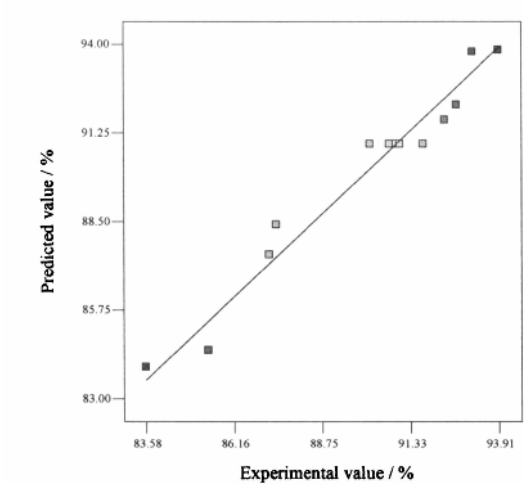

Fig. 1 Comparison of model prediction with the experimental data for decomposition rate of basic magnesium carbonate

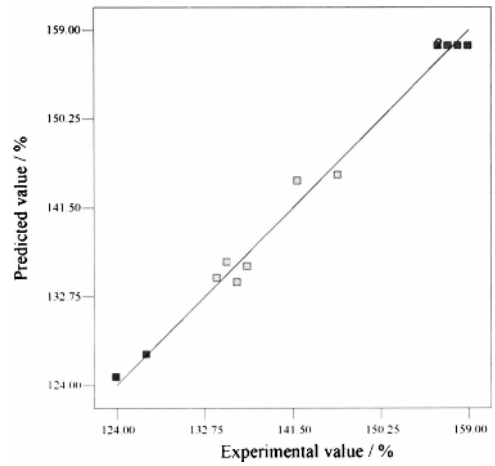

Fig. 2 Comparison of model prediction with the experimental data for activity of magnesium oxide

Fig. 1 and Fig 2 show the predicted values versus the experimental values for decomposition rate and activity of magnesium oxide. Actual response values were measured for a particular run, and the predicted values were evaluated from the model and generated by using the approximating equations. As can be seen, the predicted values obtained were quite close to the experimental values, indicating that the two models developed were reasonable.

The best way to visualize the influence of the independent variables on the response is to draw surface response plots of the model. The three-dimensional response surfaces which were constructed to show the effects of the calcination of basic magnesium carbonate variables on decomposition rate and activity of magnesium oxide using the fitted quadratic polynomial equations obtained from regression analysis was shown in Fig. 3 and Fig. 4.

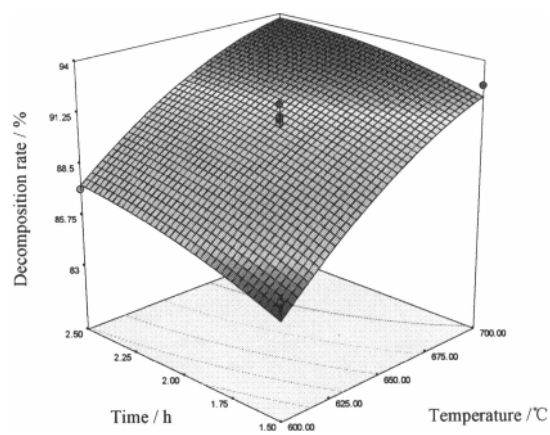

Fig. 3 Effect of calcination temperature and holding time on the decomposition rate of basic magnesium carbonate

Fig. 3 shows the effect of calcination temperature and calcination time on decomposition rate of basic magnesium carbonate. It was observed that the decomposition rate significantly increased with increasing calcination temperature and extending calcination time.

Increasing the calcination temperature up to 700℃, extending calcination time to 2.5 h gave an enhanced effect on the decomposition rate. The maximum predicated value of 93.15% was achieved at this temperature and time. The figure reveals that the effect of the calcination temperature on the field was more significant than calcination time.

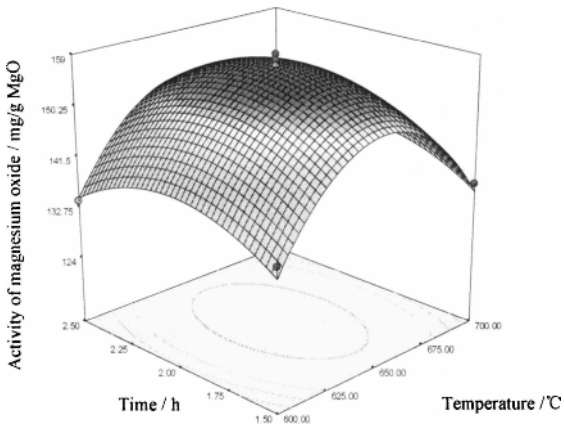

Fig. 4 Effect of calcination temperature and holding time on the activity of magnesium oxide

Fig. 4 shows the effect of calcination temperature and calcination time on activity of magnesium oxide. It was observed that the activity of magnesium oxide significantly increased with increasing calcination temperature and extending calcination time. But, when the calcination temperature was higher than 650℃ and calcination time was longer than 2 h, the activity of magnesium oxide began to decrease with the increasing of calcination temperature and extending calcination time.

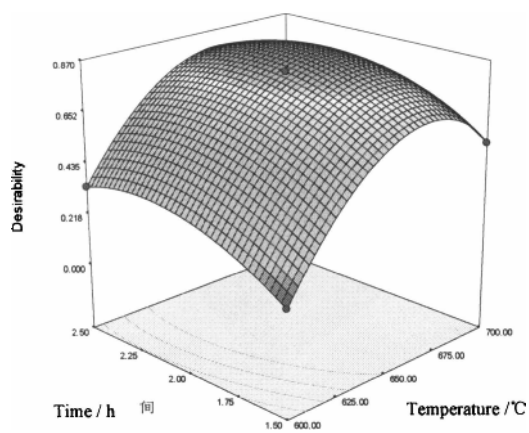

Fig. 5 Effect of calcination temperature and holding time on the comprehensive performance

Fig. 5 shows the effect of calcination temperature and calcination time on decomposition rate and activity of magnesium oxide. It was observed that the optimal condition for decomposition rate and activity of magnesium oxide was at 666.99℃and 2.12 h. The decomposition rate was 92.1971% and the activity of magnesium oxide was 155.503 mg I_2/g MgO.

Optimal Conditions and Verification of the Model

Thus, based on the above models, the optimal condition for decomposition rate and activity of magnesium oxide was at 666.99℃, 2.12 h and the decomposition rate was 92.1971%, the activity of magnesium oxide was 155.503 mg I_2/g MgO. In order to confirm the optimized conditions, the accuracy of the model was validated with experiments under conditions of optimum. An experiment was carried out with parameters as suggested by the model. The conditions used in the confirmatory experiment were as follows: calcination temperature 667℃ and calcination time 2.1 h, the giving a decomposition rate of 92.78% and activity of magnesium oxide of 155 mg I_2/g MgO (Table 5), which concurred with the model prediction. The two models, therefore, were considered to fit the experimental data very well in these experimental conditions. Therefore, the two models are acceptably valid.

Table 5 Optimum calcination conditions with model validation

Calcination temperature, x_a / ℃	Calcination time, x_b / h	Decomposition rate of basic magnesium carbonate, Y_1 / %		Activity of magnesium oxide, Y_2 / mg/g MgO	
		Predicted	Experimental	Predicted	Experimental
667	2.1	92.1971	92.78	155.503	155

XRD Analysis

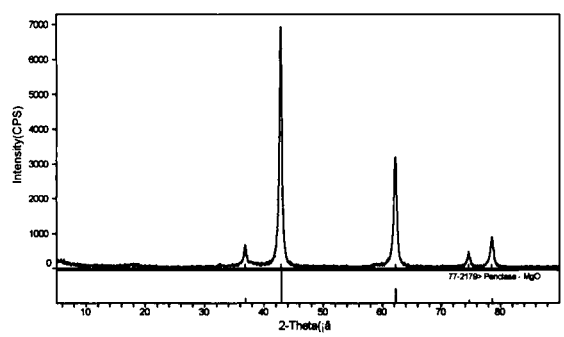

Fig. 6 The XRD pattern for the decomposition final solid products under the optimization conditions

Results of X-ray diffraction studies of the products on optimization conditions are shown in Fig. 6. The results show that magnesium oxide was the most solid product identified in which diffraction patterns satisfactorily matched with that of magnesium oxide and few decomposition products or reaction intermediates were identified in the XRD studies. Furthermore, it indicated that it is feasible to prepare magnesium oxide by calcination from basic magnesium carbonate under optimum conditions.

Conclusions

This study showed that response surface methodology was a suitable approach to optimize conditions for achieving qualified decomposition rate of basic magnesium carbonate and activity of magnesium oxide. The experimental and predicted values were very close, which reflected the correctness and applicability of RSM. Using RSM to optimize experiments, the optimal condition was found to be at 666.99℃ and 2.12 h, respectively. Under these conditions, the predicted value of decomposition rate of 92.1971%

and activity of magnesium oxide of 155.503 mg I_2/g MgO were in good agreement with the actual experimental values (92.78% and 155 mg I_2/g MgO). The magnesium oxide prepared under the optimum conditions was characterized by XRD, from which the diffraction pattern satisfactorily matched with that of the standard magnesium oxide.

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