Korean J. Chem. Eng., **20**(5), 840-843 (2003)

Maximization of Total Surface Area of Pt-SnO_2/Al_2O_3 Catalyst by the Taguchi Method

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(*Received 28 March 2003 • accepted 21 May 2003*)

Abstract−The maximization of the total surface area of Pt-SnO_2/Al_2O_3 catalyst was studied by using the Taguchi method of experimental design. The catalysts were prepared by sol-gel method. The effects of HNO_3, H_2O and aluminum nitrate concentrations and the stirring rate on the total surface area were studied at three levels of each. L_9 orthogonal array leading nine experiments was used in the experimental design. The parameter levels that give maximum total surface area were determined and experimentally verified. In the range of conditions studied it was found that, medium levels of HNO_3 and H_2O concentration and lower levels of aluminum nitrate concentration and stirring rate maximize the total surface area.

Key words: Pt-SnO_2/Al_2O_3 Catalyst, Catalytic CO Oxidation, Sol-gel Method, Taguchi Method

INTRODUCTION

Noble Metal Reducible Oxide (NMRO) catalysts are promising choices for low-temperature CO oxidation [Trimm and Onsan, 2001]. Although precipitation and impregnation are mostly used for catalyst preparation, the sol-gel method also presents a useful route for designing catalysts with well-defined microstructural properties. Since the number of parameters to be optimized in sol-gel is large and their interactions are complex [Ko, 1999], an effective experimental procedure is required.

The ultimate goal in catalyst design is maximization of activity and selectivity. However, the parameters used in catalyst design affect activity and selectivity via some physical and chemical properties such as surface area, pore structure, metal distribution and so on. Therefore, these properties should be optimized first in a way that will maximize the activity and selectivity. Since the theoretical tools are not well established in this area, the work must be heavily based on experiments. There is, however, no guarantee that optimum values of these properties will be found within the same ranges of parameters used in catalyst preparation; and even if this is the case, these ranges still may not lead to the desired activity and selectivity because of the complex characteristics of catalytic phenomena. If the experimental work is performed in full detail, the catalyst design becomes a very tedious and expensive process. Instead, the optimization of physical and chemical properties of the catalyst should be considered as "preliminary" and achieved by using as few experiments as possible. More detailed studies should be carried out for maximization of activity and selectivity in the approximate ranges that are found in these preliminary experiments. Then the surface properties and activity relationship can be established to design a more effective catalyst.

The Taguchi method, which is quite common in the design of industrial experiments, may be used for this purpose [Taguchi, 1986; Phadke, 1989]. There are some researches reported on the use of this technique in catalysis, sol-gel processes and other related areas. The examples are the works of Dawson and Barnes [1992], Wan and Chyang [1999], Sheth and Trembath [2002] and Yang et al. [2002].

If the interactions among the design parameters are neglected and error analysis is performed using some approximate techniques instead of doing additional experiments, the Taguchi method requires a significantly small number of experiments as compared with other statistical techniques [Montgomery, 2001]. Although some information is lost due to these two approximations, it is still worth choosing this approach for preliminary works considering the time-consuming nature of the sol-gel process.

This work is a part of the research on the design of a Pt-SnO_2/Al_2O_3 catalyst for low temperature CO oxidation in hydrogen-rich streams. This catalyst has the potential for CO elimination in hydrogen produced onboard of fuel cell driven vehicles. In this paper, the maximization of total surface area of Pt-SnO_2/Al_2O_3 catalysts by using the Taguchi method is presented.

EXPERIMENTAL

1. Experimental Design

Effects of four parameters, namely HNO_3, H_2O and aluminum nitrate concentration, and stirring rate, were studied since these parameters affect the sol-gel process and therefore the structure of catalyst [Rezgui et al., 1996; Ko, 1999; Schmidt, 2001]. Three levels of each parameter were chosen, as shown in Table 1. The corresponding HNO_3/AIP and H_2O/AIP mole ratios are also given in parentheses next to the concentration of HNO_3 and H_2O, respectively.

An L_9 orthogonal array as given in Table 2 was used for experi-

Table 1. Parameters and their experimental levels

Parameter	Level 1	Level 2	Level 3
(A) HNO_3 (ml)	0.65(0.02)	1.3(0.1)	2.6 (0.2)
(B) H_2O/AIP (ml)	338.4(100)	507.6 (150)	676.8(200)
(C) Aluminum nitrate (g)	5	10	17.5
(D) Stirring rate (rpm)	200	300	400

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Table 2. L_9 orthogonal array used and total surface areas measured

Experiment #	Parameter levels				Total surface area (m^2/g)	η
	A	B	C	D		
1	1	1	1	1	160.4	44.1
2	1	2	2	2	150.4	43.5
3	1	3	3	3	98.0	39.8
4	2	1	2	3	112.5	41.0
5	2	2	3	1	210.1	46.4
6	2	3	1	2	137.5	42.8
7	3	1	3	2	114.0	41.1
8	3	2	1	3	170.2	44.6
9	3	3	2	1	161.8	44.2

ments [Phadke, 1989]. This design requires nine experiments with four parameters at three levels of each. The results given in the last two column of table will be discussed later. Although this design does not have sufficient "degrees of freedom" to study "interactions" and "error estimation" in four-parameter systems, it was chosen on the basis that it required the minimum possible number of experiments. Studying interactions and error was possible only if a larger orthogonal array was used. This would increase the number of experiments significantly and diminish the advantage of the Taguchi method, as discussed in introduction. The interactions were neglected and the error was predicted by using an approximate method discussed later.

2. Catalyst Preparation

1% wt Pt, 3 wt% Sn supported on alumina was prepared by sol-gel method. The procedure by Cho et al. [1998] was modified by using aluminum nitrate to enhance gel formation. 38.43 g Aluminum Isopropoxide (AIP), 0.1985 g Pt precursor $Pt(NH_3)_4(NO_3)_2$ and 0.658 g Sn precursor $C_{16}H_{36}Sn$ were used in all runs. AIP was hydrolyzed at 358 K for 30 minutes, and the solution was peptized by adding HNO_3. After 5 minutes, Pt and Sn precursors were added to the solution which was stirred for one hour at 358 K and then placed in a 298 K water bath for 14 h, followed by aluminum nitrate addition. The alcoholic solvent was evaporated at room temperature until gel formation. The catalyst formed was oven-dried at 383 K for 48 h, calcined at 773 K for 3 h, and finally, ground and sieved to 45-60 mesh for surface area measurements. Research grade chemicals were used.

3. Total Surface Area Measurements

Total surface areas of catalysts were measured on a Micromeritics Flowsorb II-2300 by nitrogen adsorption from N_2-He mixtures by using the multipoint technique and the BET equation.

RESULTS AND DISCUSSION

The total surface areas measured are given in Table 2. The areas were measured with maximum ±5% error. These results were analyzed by the Taguchi method as described by Phadke [1989]. For a maximization problem, (i.e., larger-the-better type problems in Taguchi notation), the design equation becomes:

$$\eta = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2}\right) \quad (1)$$

where η is defined as "signal/noise ratio," and y is the response parameter that is "total surface area" in this case; n is number of measurements in each experiment which is equal to 1 in this study. As Eq. (1) shows, maximizing η is equivalent to maximizing y. Derivation and justification of Eq. (1) is beyond the objective of this paper and can be found in related references [Taguchi, 1986; Phadke, 1989]. Only necessary details will be presented through the discussions. The corresponding η for each total surface area is presented in Table 2.

1. Optimum Values of Parameters

According to the Taguchi method, the parameter levels leading to the maximum surface area can be found by using the results given in Table 2. Justification of this argument lies in the properties of L_9 and can be found in Phadke [1989], but the procedure is as follows. Assuming no interaction, the effects of parameter (i) on η can be found by comparing the average responses (M_{ij}) obtained at different levels (j). For example, the average response of B at level 1 is obtained from the results of experiments 1, 4 and 7 which have the level 1 of factor B:

$$M_{B1} = \frac{\eta_1 + \eta_4 + \eta_7}{3} = \frac{44.1 + 41.0 + 41.1}{3} = 42.1 \quad (2)$$

Similar calculations give M_{B2}=44.9, M_{B3}=42.3 indicating that level 2 of factor B should be chosen to maximize η and therefore the total surface area since it has the highest average response. The average responses for all parameters are given in Table 3 and graphical representation is shown in Fig. 1. The levels that have highest average response are underlined in Table 3. These results indicate that level 2 of HNO_3 and H_2O concentration and level 1 of aluminum nitrate concentration and stirring rate will maximize the total surface area. Since the difference between the average response of level 2 and level 3 for HNO_3 is not clear, level 3 may also be used.

Table 3. Average responses to parameter levels

Parameter	Level 1	Level 2	Level 3
(A) HNO_3 (ml)	42.5	<u>43.4</u>	<u>43.3</u>
(B) H_2O (ml)	42.1	<u>44.9</u>	42.3
(C) Aluminum nitrate (g)	<u>43.8</u>	42.9	42.5
(D) Stirring rate (rpm)	<u>44.9</u>	42.5	41.8

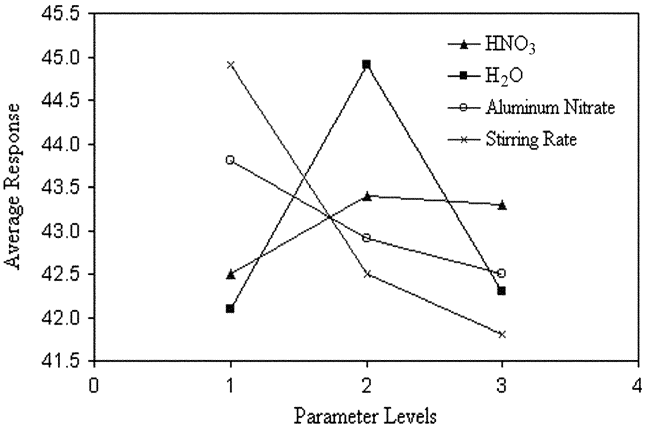

Fig. 1. Average responses to parameter levels.

2. Verification of Results

Two new catalysts (experiment 10 and 11) were prepared by using levels given in Table 3. Levels 2 and 3 of HNO_3 concentration were used in experiments 10 and 11, respectively. The levels of other parameters in both catalysts were the same as shown in Table 3. The total surface areas were found as 195.4 m^2/g in experiment 10 and 207.8 m^2/g in experiment 11. Table 1 indicates that both experiments 10 and 11 lead to much higher surface areas than all initial experiments, except experiment 5 which gave 210.1 m^2. However, it should be noted that experiments 5, 10 and 11 have comparable areas, and the same levels of A, B and D. This may indicate that best levels of A, B and D were found successfully but were identical to those in experiment 5 by chance. To test this argument and to resolve the discrepancy in the levels of C, the "no-interaction" assumptions should be checked.

Taguchi suggests the following "no interaction" model to test the existence of interactions among the parameters [Phadke, 1989]. Since M_{ij} can be treated as deviation from overall mean, $\overline{\eta}$ due to factor i at level j, the response of an experiment, for example, experiment 10, can be predicted as:

$$\eta_{predicted} = \overline{\eta} + (M_{A2} - \overline{\eta}) + (M_{B2} - \overline{\eta}) + (M_{C1} - \overline{\eta}) + (M_{D1} - \overline{\eta}) + \text{Error} \quad (3)$$

Overall mean $\overline{\eta}$ is the average response of all nine experiments and is equal to 43.1. If the model agrees with the experimental result, then the "no-interaction" assumption should be correct. However, "error" in Eq. (3) cannot be calculated directly since the number of experiments is just not sufficient as discussed earlier. Instead the "pooling technique" is used to estimate the approximate error. This technique can be summarized as "contributions of half of the degrees of freedom, which is equivalent to half of the parameters in this case, having lowest mean square in analysis of variance can be used to estimate error." Analysis of variance calculations are shown in Table 4 [Phadke, 1989].

Since A and C have the lowest mean square, their contributions can be treated as error. Then the predicted response for experiment 10 is

$$\eta_{predictiont} = \overline{\eta} + (M_{B2} - \overline{\eta}) + (M_{D1} - \overline{\eta}) = 43.1 + (44.9 - 43.1) + (44.9 - 43.1) = 46.7 \quad (4)$$

This corresponds to the total surface area of 216.5 m^2. It should be noted that model predictions for experiments 11 and 5 are the same since they have the same levels for B and D. Two conclusions can be drawn from this result. First, since the model prediction and experimental results for experiments 5, 10 and 11 are in a fair agreement, the interactions among the parameters are not very strong. Second, changing the levels of parameters A and C does not affect the area as much as B and C within the ranges of parameters studied. Since experiments 5, 10 and 11 have the same levels for B and D, their similar areas are expected. The discrepancy about the level of C between experiment 5 and two verification experiments may be attributed to its relatively low impact on the result at these conditions.

Table 4. Analysis of variance

Parameter	Degrees of freedom	Sum of squares	Mean squares
(A) HNO_3 (ml)	2	1.54	0.77
(B) H_2O (ml)	2	14.59	7.30
(C) Aluminum nitrate (g)	2	2.88	1.44
(D) Stirring rate (rpm)	2	15.85	7.93
Error	0	0	
Total	8	34.86	

CONCLUSIONS

To maximize the total surface area, HNO_3 (A) should be at medium or high level in the range used, while H_2O (B) should be at its medium level. Although the model suggests the lowest level of aluminum nitrate (C), higher levels of this parameter seem to produce similar results. The stirring rate (D) should be at its lowest level to increase total surface area. ANOVA results show that B (H_2O concentration) and D (stirring rate) are most significant factors affecting the total surface area with the same level of contribution.

On the other hand, the model prediction of "insignificant interactions" should be treated in terms of "overall" impact of parameters on the resulting total surface area. It is quite unlikely that interactions are insignificant if the individual reactions in the sol-gel process are considered. As a matter of fact, HNO_3, H_2O and aluminum nitrate concentrations affect the properties of catalyst via changing the balance between hydrolysis and condensation reactions in the sol-gel process in an interacting manner [Rezgui et al., 1996; Ko, 1999; Schmidt, 2001]. Even the high apparent significance of stirring rate may be partially due to these interactions since the experimental design used here is not sufficient to separate the interactions from the main factor effects. Therefore, a more detailed experimental design including interactions among the parameters should be used to explain the impacts of parameters on the physical and chemical phenomena in sol-gel. This was not intended in this work. Instead, it was sufficient to locate the best levels of parameters to maximize the total surface area by using as few experiments as possible and using these findings for further studies. It can be also concluded that Taguchi method may be utilized for catalyst design to reduce time and efforts needed.

ACKNOWLEDGMENT

This project was supported by Bogazici University Research Fund through Project No: 01HA502 and The Scientific and Technical Research Council of Turkey through Project No: MISAG-228.

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