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# Process optimization on reaction between 3-mercaptopropyl trimethoxysilane (MPTMS) and mesoporous silica using response surface methodology

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**ABSTRACT**

*3-Mercaptopropyl Trimethoxysilane (MPTMS) is a common silane coupling agent and can fix ionic liquid on supporter in supported ionic liquid catalyst field. In this study, response surface methodology was used to design and optimize the reaction conditons which were MPTMS dosage, reaction time and temperature for the best MPTMS loading amount (S content). The optimum experimental conditions are MPTMS 1.43 g, time 31 h and temperature 391 K. The predicted S content is 0.95 mmol/g and the experimental is 0.91 mmol/g. The thickness of MPTMS layer is about 0.55 nm in $SiO_2$ pore.*

**Key words**: Response surface methodology; mesoporous silica; supporter; silane coupling agent

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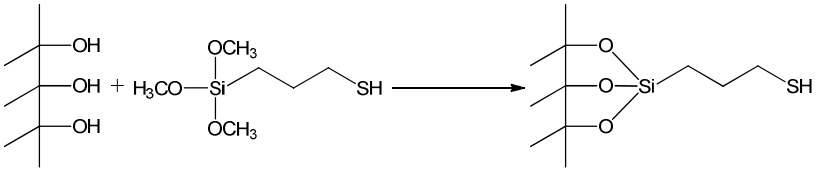
## INTRODUCTION

Nowadays, supported ionic liquid catalyst (SILC) can be employed in many classical oragnic synthesis[1，2]. For example, Lina Han et al used porous polymer bead-supported ionic liquids for the synthesis of cyclic carbonate from $CO_2$ and epoxide [3]. Matthias Josef Beier et al used ionic liquid supported Pt nanoparticles as catalyst for enantio-selective hydrogenation [4]. Majid Vafaeezadeh et al used silica suported task specific ionic liquid catalyst system for oxidation of cyclohexene to adipic aicid with 30% $H_2O_2$ [5].

In previous study of SILC, functionalized ionic liquids should be conjuncted on the special materials. Mesoporous silica ($SiO_2$) has the right space for catalysis and widely uses in SILC as carrier [6]. 3-Mercaptopropyl Trimethoxysilane (MPTMS) is a common silane coupling agent and can fix ionic liquid on supporter [7]. However, the quantitative research for the reaction between MPTMS and mesoporous silica has no relevant reports. The reacton equation is shown in Eq.1:




(1)

Response surface methodology (RSM) is a kind of optimization method and has a good application in the design of experiments, data analysis and experimental prediction [8, 9]. So, I this paper, the effects of MPTMS dosage, reaction time and temperature were investagated on the MPTMS loaded on mesoporous $SiO_2$. RSM was used to search the best MPTMS loading at a optimal reaction conditon.

## EXPERIMENTAL SECTION

### 2.1 Synthesis and characterization of MPTMS-$SiO_2$

Firstly, 5g mesoporous silica ($SiO_2$), 3-mercaptopropyl trimethoxysilane (MPTMS) and 50mL toluene were added in 100 mL stainless steel hydrothermal reactor with PTFE lining. Average porous size and surface area of mesoporous silica are 9.4nm and 329.8$m^2$/g, respectively. Toluene is AR and MPTMS (97%, CP) was purchased from Acros Organics (Geel, Belgium). Secondly, hydrothermal reactor was placed in blast oven which could adjust reaction temperature. After a period of time, hydrothermal reactor was removed form oven and cooled by air. Thirdly, MPTMS-$SiO_2$ was obtained using solid-liquid separation. The sample was dryed by blast oven. Finally, sulfur (S) contents of the samples were analyzed by elemental analyzer. Sulfur content is equivalent to the loading of MPTMS on mesoporous. Elemental analyzer is used GERMANY ELEMENTAR VARIO EL Ⅲ. Nitrogen adsorption-desorption isotherms were determined at 77K using an autosorb IQ porosimeter. Prior to measurement, the sample was degassed at 200$^o$C for 2 h. Specific surface areas and pore distributions were calculated using the BET (Brunauer-Emmett-Teller) and NLDFT (nonlocal density functional theory) methods, respectively.

### 2.2 Response surface methodology

**Table 1 Levels of the variables for BBD experimental design**

| Variable | Code | Unit | Levels | | |
|---|---|---|---|---|---|
| | | | -1 | 0 | 1 |
| MPTMS | A | g | 1 | 1.3 | 1.6 |
| Time | B | hour | 12 | 24 | 36 |
| Temperature | C | K | 353.13 | 373.13 | 393.13 |

Tab.1 lists range of three independent variables. RSM analyzed the experimental data obtained from above procedure by the following second-order polynomial as shown by Eq.2 [10]:

$$S = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} x_i^{\,2} + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \beta_{ij} x_i x_j \qquad (2)$$

S is the predicted response. The $x_i$ and $x_j$ are independent variable. The $\beta_0$ is the regression intercept and $\beta_i$, $\beta_{ii}$, $\beta_{ij}$ are the regression coefficient. Design Expert software version 8.06 was used to perform the regression analysis and analysis of variance (ANOVA). Using regression analysis to get the fitted quadratic polynomial equation, and then use the equation to develop the response surfaces and contour plots.

**Table 2 Experimental design matrix and results for process optimization**

| Run | MPTMS / g | Time /hour | Temperature /K | S / mmol/g | |
|---|---|---|---|---|---|
| | | | | Experimental | Predicted |
| 1 | 1.6(1) | 24(0) | 353.15(-1) | 0.798 | 0.803 |
| 2 | 1.0(-1) | 12(-1) | 373.15(0) | 0.746 | 0.706 |
| 3 | 1.3(0) | 24(0) | 373.15(0) | 0.919 | 0.91 |
| 4 | 1.3(0) | 24(0) | 373.15(0) | 0.902 | 0.91 |
| 5 | 1.0(-1) | 36(1) | 373.15(0) | 0.712 | 0.706 |
| 6 | 1.0(-1) | 24(0) | 393.15(1) | 0.723 | 0.715 |
| 7 | 1.0(-1) | 24(0) | 353.15(-1) | 0.766 | 0.763 |
| 8 | 1.3(0) | 36(1) | 393.15(1) | 0.894 | 0.905 |
| 9 | 1.6(1) | 24(0) | 393.15(1) | 0.918 | 0.919 |
| 10 | 1.3(0) | 24(0) | 373.15(0) | 0.911 | 0.91 |
| 11 | 1.6(1) | 36(1) | 373.15(0) | 0.922 | 0.908 |
| 12 | 1.3(0) | 24(0) | 373.15(0) | 0.915 | 0.91 |
| 13 | 1.3(0) | 24(0) | 373.15(0) | 0.908 | 0.91 |
| 14 | 1.6(1) | 12(-1) | 373.15(0) | 0.794 | 0.798 |
| 15 | 1.3(0) | 36(1) | 353.15(-1) | 0.847 | 0.853 |
| 16 | 1.3(0) | 12(-1) | 353.15(-1) | 0.854 | 0.841 |
| 17 | 1.3(0) | 12(-1) | 393.15(1) | 0.865 | 0.857 |

## RESULTS AND DISCUSSION

### 3.1 Experimental results

According to the Box-Behnken Design (BBD), experimental values of S contents at different experimental conditons are shown in Tab.2. From the Tab.2, there are 17 experimental points which contain 12 factorial points and 5 zero ponits. 12 factorial points are three levels (A,B,C) to form vertices of cube. Zero ponits are the center of

the cube. Experimantal error is estimated by 5 zero ponit experiments.

### 3.2 Model and significant test

Experimental data was fitted by binary regression using Design-Expert Software. The fitting result is as shown in Eq.3, which takes their coded value.

$$S=0.91+0.061A+0.015B+0.017C+0.04AB+0.041AC+0.009BC-0.091A^2-0.027B^2-0.019C^2 \quad (3)$$

Predicted values of S contents were caculated by Eq.3. The caculated results are shown in Tab.2 and predicted and experimental values are very close.

**Table 3 Results for the reduced quadratic model of the variable effects on the response**

| Source | Sum of squares | f | Mean square | F-Value | Prob>F | Significant |
|---|---|---|---|---|---|---|
| Model | 0.088 | 9 | 9.83E-3 | 70 | <0.0001 | Significant |
| A-MPTMS | 0.029 | 1 | 0.029 | 209.33 | <0.0001 | Significant |
| B-Time | 1.68E-3 | 1 | 1.68E-3 | 11.97 | 0.0105 | Significant |
| C-Temperature | 2.28E-3 | 1 | 2.28E-3 | 16.22 | 0.0050 | Significant |
| AB | 6.56E-3 | 1 | 6.56E-3 | 46.71 | 0.0002 | Significant |
| AC | 6.64E-3 | 1 | 6.64E-3 | 47.29 | 0.0002 | Significant |
| BC | 3.24E-4 | 1 | 3.24E-4 | 2.31 | 0.1726 | |
| $A^2$ | 0.035 | 1 | 0.035 | 246.19 | <0.0001 | Significant |
| $B^2$ | 3.04E-3 | 1 | 3.04E-3 | 21.65 | 0.0023 | Significant |
| $C^2$ | 1.54E-3 | 1 | 1.54E-3 | 10.96 | 0.0129 | Significant |
| Residual | 9.83E-4 | 7 | 1.41E-4 | | | |
| Lack of Fit | 8.13E-4 | 3 | 2.71E-4 | 6.38 | 0.0527 | No significant |
| Pure Error | 1.7E-4 | 4 | 4.25E-5 | | | |

*$R^2$=0.9890, Adj-$R^2$=0.9749, Pred R-Squared=0.8516, Adequate Precision=23.39, CV=1.4%。*

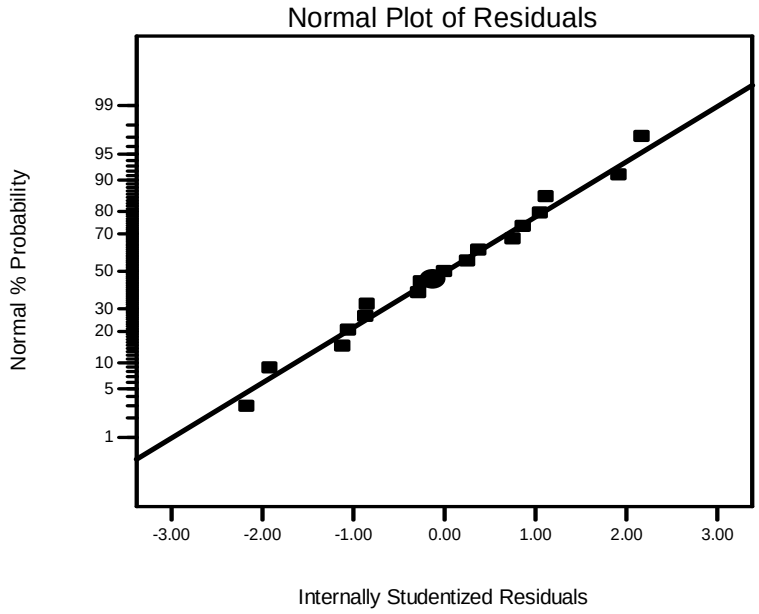



**Figure 1 Normal plot of residuals for S content**

Analysis fo variance is shown in Tab.3. The Model F-value of 70.00 implies the model is significant. There is only a 0.01% chance that a Model F-Value this large could occur due to noise. Values of Prob > F less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, AC, $A^2$, $B^2$, $C^2$ are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. According to the Prob > F value, the order of influence on the each factor level in the selected range is MPTMS>Temperature>Time. The Lack of Fit F-value of 6.38 implies there is a 5.27% chance that a Lack of Fit F-value this large could occur due to noise. This relatively low probability (<10%) is troubling. The coefficient of determination ($R^2$) is excellent at 0.9890. A high $R^2$ value indicates that the obtained model gives a good system response estimates within the studied range. The Pred R-Squared of 0.8516 is in reasonable agreement with the Adj R-Squared of 0.9749. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 23.39 indicates an adequate signal. Also, a relatively lower value of the coefficient of variation (CV of 1.4%) indicates a better precision and reliability of the exeprimental rauns. The CV which is a ratio of the standard error of estimate to the mean value of the observed response is a measure of reproducibility of the model. As a general rule, a model can be considered reasonable reproducible if its CV is not

greater than 10% [11].

Two diagnostic figures are analyzed to check on the models adequacy, which are shown in Fig.1. From the Fig.1, it is shown the normal plot of residuals for reaction between MPTMS and mesoporous $SiO_2$, which expresses the residuals fall on a straight line. The straight line indicates that errors in this study are distributed normally for all the responses. Fig.2 shows the plot of residuals versus preidicted S content. The figure indicates a similar random scatter without any obious patterns and unusual structrue. This result means the model is adequat. It can be concluded that the model is able to successfully capture the correlation between the the experimental conditions and S content [11].

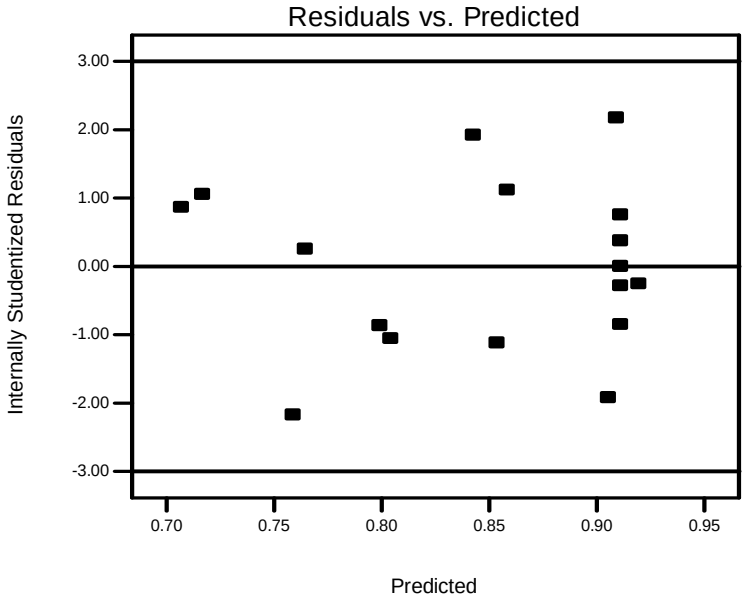
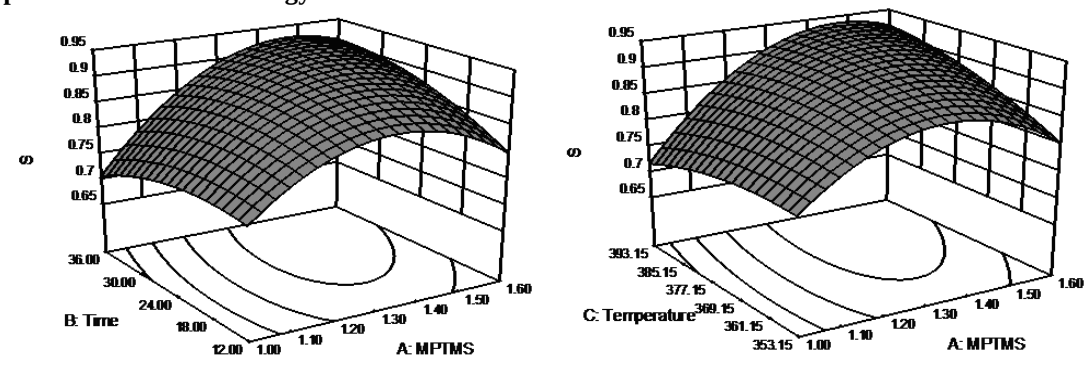



**Fig. 2 Residuals versus predicted for S content.**

### 3.3 Response surface methodology




**(a)** **(b)**

**Fig.3 Three-dimensional response surface plot of S content for reaction between MPTMS and mesoporous $SiO_2$**

Fig.3(a) shows three-dimensional response surface figure on the effect of the MPTMS (A) dosage and time (B) for S contens. When the MPTMS and time are fixed on zero level, curves of S content express increasing trends firstly and then decreasing. It is implied the there are the best experimental conditions. From the Fig.3(b), it is shown three-dimensional response surface figure on the effect of the MPTMS (A) dosage and Temperature (C) for S contens. It is clearly to see that temperature experimental conditon appears the best value. Accoding to the Fig.2(a) and Fig.2(b), the optimum experimental conditions are MPTMS 1.43 g, time 31 h and temperature 391 K and predicted S content is 0.95 mmol/g. Using the optimun conditons, the experimental S content is 0.91 mmol/g. The experimental value obtained is very close with the value calculated form the model, which consequently verifies the model capability.

### 3.4 $N_2$ adsorption and desorption

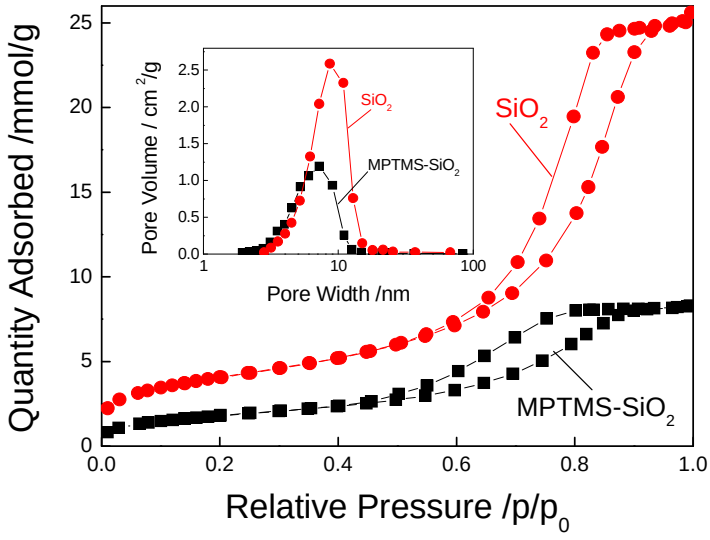



**Fig.4 $N_2$ adsorption-desorption isotherms and pore diameter distributions of $SiO_2$ and MPTMS-$SiO_2$**

Fig.4 shows the $N_2$ adsorption-desorption isotherms and pore diameter distributions of $SiO_2$ and MPTMS-$SiO_2$. BJH distributions and BET surface were calculated using $N_2$ adsorption at 77K. Both of samples displayed a type IV isotherm with HI hysteresis loop and a sharp in crease in pore volume adsorbed above $P/P_0$~0.9, which is typical characteristic of highly ordered mesoporous materials [12]. MPTMS significantly affected the surface area and pore distribution of MSG and pore volume is significantly smaller. The $SiO_2$ sample showed a maximum pore diameter at 9.4 nm and surface area of 329.8 m²/g. After reaction, the maximum pore diameter and surface area of MPTMS-$SiO_2$ decreased to 8.3 nm and 210.6 m²/g, respectively. The thickness of MPTMS layer is about 0.55 nm in $SiO_2$ pore.

## CONCLUSION

The best expeimental conditons was aquired about the reaction between MPTMS and mesoporous $SiO_2$ using response surface methodology. The optimum experimental conditions are MPTMS 1.43 g, time 31 h and temperature 391 K. The predicted S content is 0.95 mmol/g and the experimental is 0.92 mmol/g. The thickness of MPTMS layer is about 0.55 nm in $SiO_2$ pore.

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