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利用 Taguchi 法以高岭土为原料制备高硅 NaY 分子筛

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摘要:采用 Taguchi 试验方法优化出了以高岭土为原料制备高硅 NaY 分子筛的最佳合成参数,考察了硅溶胶的加入量、反应体系的碱度、加水量以及晶化时间对 NaY 分子筛硅铝比和结晶度的影响。结果表明,高硅 NaY 分子筛的最佳合成条件是:反应体系各组分的物质的量比为 $7.5SiO_2$:$1.0Al_2O_3$:$2.2Na_2O$:$120H_2O$,晶化时间为 16 h。同时发现,对合成样品性能的影响最为显著的因素是硅溶胶的加入量和碱度。采用 X 射线衍射、N_2 静态容量吸附法和扫描电镜对利用最佳条件所合成样品的硅铝比、比表面积、孔分布以及表观形貌进行了表征。结果显示,以高岭土原料制备的 NaY 分子筛比参考样品拥有更高的硅铝比和更大的比表面积。

关键词:高岭土;NaY 分子筛;硅铝比;结晶度;Taguchi 技术

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Synthesis of High-Silica NaY Zeolite from Kaolin Based on Taguchi Technology

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Abstract: This paper reports a study of using Taguchi technology to find the optimum parameters for the synthesis of high-silica Y-zeolite from kaolinite. The effects of additional silica source, alkali, distilled water, and crystallization time on the synthesis of high Si/Al zeolite Y were investigated. The results show that the dosage of additional silica source(silica sol) and alkali are the most influential factors on the synthesis of high-silica Y zeolite. The optimum preparation conditions are that the molar composition of sodium aluminosilicate gel is $7.5SiO_2$:$1.0Al_2O_3$:$2.2Na_2O$:$120H_2O$, and crystallization time is 16 h. The NaY zeolite synthesized at optimized conditions was characterized by X-ray diffraction (XRD), N_2 adsorption-desorption techniques and Scanning electron microscope (SEM). The characterization results indicate that the sample has higher Si/Al ratio and larger surface area than the reference Y zeolite sample.

Key words: kaolinite; NaY zeolite; Si/Al ratio; relative crystallinity; taguchi technology

Y zeolite with faujusite(FAU) framework is widely used in modern petrochemical industry[1], especially as a catalytic component, playing great role in the fluid catalytic cracking(FCC) process. At present, the dominant commercial Y zeolite is the low silica zeolite product, of which the acidity, thermal and hydrothermal stability are rather limited[2,3]. With the feedstocks of FCC being heavier, poorer in quality and the trend of in-

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creasing use in liquefied petroleum gas(LPG), gasoline and diesel, the zeolite Y has to be ultrastablized in steam at 700 ℃ to meet the special requirements in acidity and hydrothermal stability. It is well known that the higher the Si/Al ratio, the more stable the structure of the Y zeolite. The use of high-silica zeolite Y can noticeably improve its structure stability at high temperature[4], in addition to the higher thermal stability, the zeolite exhibits a much higher catalytic activity and selectivity than the low silica Y molecular sieves[5]. Present octane-barrel catalysts usually consist of ultrastable, steam dealuminated Y zeolite on an active matrix. Such a steam modification is a highly energy cost approach. Other chemical modifications, such as extraction by acid complexation or secondary synthesis using $SiCl_4$ and $(NH_4)_2SiF_6$[6], citric acid[7,8], are not environmental friendly processes. Therefore, using *in-situ* technique to directly prepare high-silica zeolite Y has received much attention because this technique makes NaY zeolite overgrowing in metakaolin and consumes much less energy and is environmentally benign [9,10]. However, for the synthesis of high-silica Y zeolite from kaolin using in-situ method, there are many parameters to be considered in affecting the framework Si/Al ratio. Besides, these parameters influence one another. Hence, the analyses using conventional experimental method are inefficient. Therefore, a technique called Taguchi robust method is applied in this work, which is based on statistical design and offers a simple efficient approach to optimize designs for performance, quality and cost [11~15]. This is a powerful tool to obtain the optimum conditions in the synthesis of high-silica zeolite[16~18]. The objective of this work is to prepare high-silica NaY zeolite from kaolin using Taguchi method, and to evaluate the effect of a few factors on Si/Al ratio and crystallinity.

1 Experimental design and procedure

1.1 Raw materials

Kaolin clay (containing 45.75wt% SiO_2 and 39.70wt% Al_2O_3) was supplied by ZiBo Hi-King Powder Material Technology Co., Ltd. In order to increase the Si/Al ratio of Y zeolite product, the silica sol purchased from HengShengDa Chemical Co., Ltd. of Qingdao, China with a composition of approximately 25% SiO_2 and 0.3% Na_2O was used as additional silica source. The sodium hydroxide(containing 96.0wt% NaOH, Laboratory Reagent(L.R.) grade) was purchased from Beijing Yili Chemicals Co. The sodium aluminate (containing 41.0wt% Al_2O_3) was purchased from Sinopharm Chemical Reagent Co., Ltd.

1.2 Zeolite crystallization

1.2.1 Thermal activation of kaolin

The kaolin clay as the starting material was calcined at 720 ℃ for 4 hours at a heating rate of 15 ℃·min^{-1} in a muffle furnace to obtain the metakaolin.

1.2.2 Preparation of structure directing agent

The structure directing agent was prepared by mixing appropriate amounts of sodium hydroxide, sodium aluminate, silica sol and distilled water under stirring. Then the resulting mixture with a molar ratio of $17SiO_2$:$1.0Al_2O_3$:$17Na_2O$:$350H_2O$ was aged at 40 ℃ for a period of about 6 hours. The resulting solution was the self-made structure directing agent.

1.2.3 Synthesis of high-silica NaY zeolite

Zeolite Y was synthesized by hydrothermal method with the above structure directing agent, which functions as nucleation centers (seeds) in the synthesis process. The sodium aluminosilicate gel was prepared according to the gel composition listed in Table 1. Firstly, sodium hydroxide and distilled water

Table 1　$L_9(3^4)$ orthogonal arrays

Experiment No.	SiO_2	NaO_2	H_2O	Time / h
1	7.0	2.2	100	16
2	7.0	2.4	120	20
3	7.0	2.6	140	24
4	7.5	2.2	120	24
5	7.5	2.4	140	16
6	7.5	2.6	100	20

Continued Table 1

7	8.0	2.2	140	20
8	8.0	2.4	100	24
9	8.0	2.6	120	16

were mixed to form alkali solution and then metakaolin was added to the alkali solution and stirred for 1 h to form slurry. Afterwards, structure directing agent was added dropwise into the above slurry, and stirred vigorously until uniform gel was obtained. The resulting mixture was transferred into an autoclave, where the hydrothermal crystallization was carried out at 373 K for 16~24 h. Finally, after the completion of crystallization, the samples were filtered, washed with distilled water until pH=7~8, and dried at 373 K overnight.

1.3 Design of experiments

In this work, four synthesis parameters: dosage of additional silica source (factor A), alkali dosage (factor B), the amounts of distilled water(factor C) and crystallization time(factor D) were chosen to study their impact on the relative crystallinity of high-silica Y zeolite. Table 2 shows the factors and their levels. The selection of the orthogonal array is based on the synthesis condition and the parameters, in the present investigation, $L_9(3^4)$ orthogonal array was chosen and shown in Table 2 which has 9 rows and 4 columns. It can be seen that this experiment requires nine tests with four parameters at three levels of each. Although this Taguchi design does not have sufficient "degrees of freedom" to study "interactions" and "error estimation" in four parameters system, the optimal control factors can be obtained from a minimum possible number of experiments without consideration of the interactions.

Table 2 Control factors and levels for synthesis of high Si/Al NaY zeolite

Control factor	(A) SiO_2 / mol	(B) NaO_2 / mol	(C) H_2O / mol	(D) Crystallization time / h
Level 1	7.0	2.20	100	16
Level 2	7.5	2.40	120	20
Level 3	8.0	2.60	140	24

1.4 Characterization

The relative crystallinity and crystal phase of the samples were characterized by powder X-ray diffraction (XRD) using PANlytical XPert PRO MPD X-ray Diffractometer with a nickel-filter and Cu $K\alpha$ radiation (λ=0.154 06 nm) generated at 40 kV, 30 mA, at a scanning speed of $2°\cdot min^{-1}$ and in the 2θ range of 5°~70°. The diffraction peak intensities were measured using flicker recording.

For the zeolite Y, the crystallinity was calculated by comparing the intensity of the definite peaks in the XRD pattern to that of pure faujasite. The Si/Al ratio was also determined by X-ray diffraction according to the following relationship:

$$Si/Al = (2.593\,5 - a_0)/(a_0 - 2.421\,2)$$

where a_0 is cell parameters.

Micromeritics ASAP 2010 system was used to characterize the surface area and pore-structure of the Y zeolite samples using N_2 sorption under 77.3 K. The samples were degassed at 573 K overnight before measurements. The particle size and morphology of the samples were determined by scanning electron microscopy(SEM) on a FEI Sirion 200 operated at an acceleration voltage of 20 kV. For comparison purposes, a commercially available Y-zeolite was used as reference sample in this study.

2 Results and discussion

Taguchi method was used to optimize the parameters with the most principal influence on the framework Si/Al molar ratio and the crystallinity of NaY zeolite from kaolin. The signal-to-noise ratio (S/N) of the response analysis was used to measure the quality characteristic deviation from the desired value.

2.1 The signal-to-noise ratio (S/N) analysis

The analysis of the Taguchi data was carried out

using statistical software "MINITAB 13". In order to estimate the influence of each factor on the responses, the signal-to-noise ratio for each factor must be calculated(Table 3). The appropriate S/N ratio must be chosen before using the software to analyze the results. Generally, three signal-to-noise ratios: smaller-the-better, "larger-the-better", "nominal-the-best", were used for the optimization of static problem. It has been accepted that the higher Si/Al molar ratio, the better thermal stability of the NaY zeolite. Therefore, in the study, the S/N ratio was chosen by the analysis for the problem of larger-the-better, and the signal-to-noise ratio of each experiment was calculated by the following formula[19]:

$$\frac{S}{N} = -10\lg[\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2}] \quad (1)$$

Where n is the number for each experiment, n=1 in this work, y_i is the Si/Al molar ratio or the crystallinity of Y zeolite.

Table 3　Experimental data and S/N ratio for Si/Al ratio and relative crystallization of NaY zeolite

Exp.no.	S/N ratio as a function of Si/Al ratio		S/N ratio as a function of Relative crystallinity	
	Si/Al ratio	S/N ratio / dB	Relative crystallinity / %	S/N ratio / dB
1	4.7	13.44	81.86	38.26
2	4.2	12.46	63.80	36.10
3	4.3	12.66	76.95	37.72
4	5.4	14.65	86.22	38.71
5	4.9	13.80	82.76	38.36
6	4.5	13.06	83.45	38.43
7	5.0	13.98	80.59	38.13
8	4.7	13.44	78.37	37.88
9	4.8	13.62	87.22	38.81

Table 3 lists the signal-to-noise ratio for the Si/Al ratio and relative crystallization of Y-type zeolite calculated by equation (**1**). The mean S/N ratio for each level of the factors is summarized and the S/N response table for the Si/Al ratio and relative crystallinity is shown in Table 4 and 5, respectively. As shown in Table 4 and 5, additional silica source(factor A) is the most important parameter affecting the Si/Al ratio and relative crystallization of Y-type zeolite. The second influential one is alkali (factor B), then followed by crystallization time (factor D) and distilled water(factor C). Fig.1 and Fig.2 present the S/N response graph for the Si/Al ratio and crystallinity, respectively, which were obtained by means of MINITAB 13 statistical software. In general, the larger the S/N ratio, the larger contribution of one

Table 4　S/N response table for Si/Al ratio

Parameters	Mean S/N ratio(dB) for Si/Al ratio				
	Level 1	Level 2	Level 3	δ	Rank
A	12.85	13.84	13.68	0.98	1
B	14.02	13.23	13.11	0.91	2
C	13.31	13.58	13.48	0.26	4
D	13.62	13.17	13.58	0.45	3

Table 5　S/N response table for relative crystallinity

Parameters	Mean S/N ratio(dB) for Crystallinity				
	Level 1	Level 2	Level 3	δ	Rank
A	37.36	38.50	38.27	1.14	1
B	38.37	37.45	38.32	0.92	2
C	38.19	37.87	38.07	0.32	4
D	38.48	37.55	38.10	0.92	3

control factor at that level for the Si/Al ratio and relative crystallization of NaY zeolite. Therefore, as shown in Fig.1 and Fig.2, the optimum synthesis conditions for this experiment are A at level 2, B at level 1, C at level 2, and D at level 1.

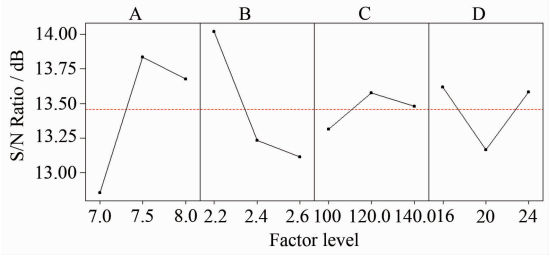

Fig.1 S/N response graph of framework Si/Al ratio

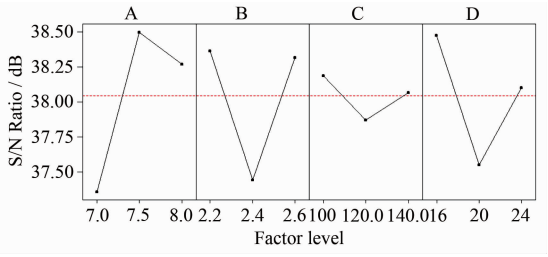

Fig.2 S/N response graph of relative crystallinity

2.2 Analysis of variance(ANOVA)

We have discussed earlier that the L_9 orthogonal array do not have enough "degrees of freedom" for error estimation in four-parameter system. Hence, it is necessary to choose one parameter to estimate the error. Since factor C possess the lowest mean square and has the minimum influence on the synthesis of high silica Y zeolite, its contribution can be treated as error. The main objective of ANOVA is to find the key design parameter affecting zeolite structure. Table 6 and 7 show the ANOVA results for the Si/Al ratio and crystallinity of Y zeolite, respectively. It can be observed from Table 6 that the amount of additional silica source (factor A, p=44.83%) has the highest contribution to the Si/Al ratio of Y zeolite. The alkali (factor B, p=41.15%) has the second highest contribution. The contribution of crystallization time (factor D) is just 10.12%, and the effect of crystallization time has very small contribution to the Si/Al ratio of Y zeolite. Table 7 demonstrates the contribution(p) of each factor to the total variation, indicating their influential degrees on crystallinity. The results show that additional silica source (p=42.46%), alkali(p=30.88%), and crystallization time(p=24.88%), all have a significant influence on the crystallinity of zeolite samples.

Table 6 Analysis of variance (ANOVA) for framework Si/Al ratio

Source	SS	DF	Variance	F	p / %
A	0.482 22	2	0.241 11	11.42	44.83
B	0.442 22	2	0.221 11	10.47	41.15
D	0.108 89	2	0.054 44	2.58	10.12
Error	0.042 22	2	0.021 11		3.93
Total	1.075 56	8			100

Note: SS, sum of squares; DF, degree of freedom; F, F ratio of the factor; p, percentage of contribution.

Table 7 Analysis of variance(ANOVA) for relative crystallinity

Source	SS	DF	Variance	F	p / %
A	164.871	2	82.436	23.83	42.46
B	119.947	2	59.974	17.34	30.88
D	96.642	2	48.321	13.97	24.88
Error	6.918	2	3.459		1.78
Total	388.379	8			100

Note: SS, sum of squares; DF, degree of freedom; F, F ratio of the factor; p, percentage of contribution.

2.3 Prediction and confirmation

The optimal synthesis parameters were obtained from above investigations. To reconfirm the optimal conditions, Taguchi method also offers a way to predict and verify the improvement of the quality characteristics using the optimal level of the parameters. The S/N

ratio can be predicted by the following relationship[20]:

$$S/N_{Predicted} = \overline{S/N} + (S/N_{A2} - \overline{S/N}) + (S/N_{B1} - \overline{S/N}) + (S/N_{C2} - \overline{S/N}) + (S/N_{D1} - \overline{S/N})$$

Where $\overline{S/N}$ is the mean S/N ratio of all nine experiments and equal to 13.46, S/N_{A2}, S/N_{B1}, S/N_{C2}, S/N_{D1} is the mean S/N ratio at the optimal level, and their values are 13.84, 14.02, 13.58, and 13.62, respectively. The predicted response for the Si/Al ratio of Y zeolite is calculated to be 14.68 using the above equation. Accordingly, the Si/Al ratio can also be estimated to be 5.42 using the following formula: $14.68 = -10\lg(1/y^2)$. On the other hand, the predicted response for the relative crystallinity is 39.42(dB), and the crystallinity is 93.54%. The verification experiment was performed using the optimal conditions as A2, B1, C2, D1, the framework Si/Al ratio of Y zeolite in this experiment is 5.5 and the relative crystallinity is 88.35%. According to the experimental results, it can be found that there is a quite consistent conclusion between the predicted and experimental Si/Al ratio. This indicates that the Taguchi approach does well in optimizing synthesis parameters to improve the Si/Al ratio and relative crystallinity of Y-type zeolite.

2.4　Characterization of high-silica NaY zeolite

Here in this work, the high-silica NaY zeolites were obtained at the optimal conditions. For comparison purposes, we chose a commercial NaY zeolite as a reference sample. Fig.3 shows XRD patterns of the high-silica Y zeolite and the commercial zeolite. It can be seen that both of the two samples display strong and typical characteristic diffraction peaks of zeolite Y, indicating high crysallinity. Their crystalline structure is of faujasite-type zeolite. Fig.3 also indicates that the high-silica Y zeolite has higher framework Si/Al molar ratio(5.5) than the commercial one. It is well known that the pore characteristic of Y zeolite is one of the most important factors influencing FCC catalytic performance. Table 8 lists surface area and pore-structure parameters of these two zeolite samples. Compared to the commercial Y zeolite, the high-silica NaY zeolite has a larger BET surface area, micropore area and higher Si/Al ratio, but its total pore volume, micropore volume is similar to those of the commercial zeolite. In addition, Table 8 also indicates that these two Y zeolite samples possess narrow micropore size distribution centered around 0.53 nm. Fig.4 presents the SEM im-

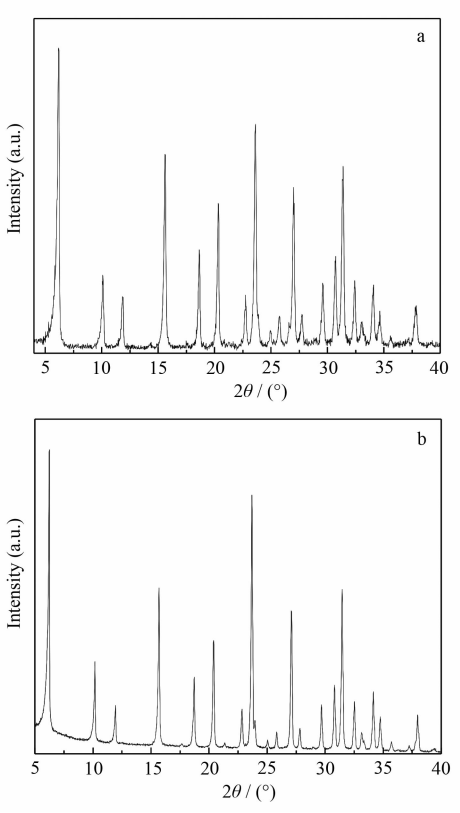

Fig.3　XRD pattern of the high-silica NaY zeolite (a) and the commercial zeolite (b)

Table 8　Surface area and pore-structure parameters of the two Y zeolites

Sample	High-silica Y zeolite	Commercial Y zeolite
BET surface area / ($m^2 \cdot g^{-1}$)	709	662
Micropore area / ($m^2 \cdot g^{-1}$)	683	628
Total pore volume / ($cm^3 \cdot g^{-1}$)	0.36	0.37
Micropore volume / ($cm^3 \cdot g^{-1}$)	0.34	0.33
Micropore size / nm	0.53	0.57
Si/Al ratio	5.5	4.0
Relative crystallinity / (%)	88.3	88.0

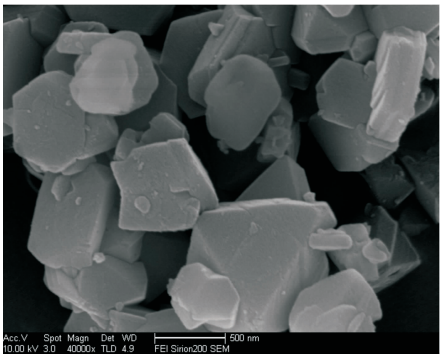

Fig.4 SEM image of high-silica NaY zeolite

age of NaY zeolite synthesized at optimum synthesis conditions. As shown in Fig.4, the particle size is narrowly distributed in the range of 0.5~1.0 μm.

3 Conclusions

The pure Y-type zeolite with high Si/Al ratio(5.5) and high crystallinity was prepared via *in-situ* synthesis from kaolin. The optimal conditions were obtained based on Taguchi approach with $L_9(3^4)$ orthogonal array. The verification experiment confirms the optimization results.

(A) According to Taguchi method, the amount of additional silica source has the strongest effect on the framework Si/Al ratio and relative crystallinity of NaY zeolite. Alkali and crystallization time have minor effect, and the amount of distilled water has the lowest effect on framework Si/Al ratio.

(B) For such $L_9(3^4)$ orthogonal array with four parameters at three levels of each, the interactions were not considered, and the contribution from the amounts of distilled water was treated as error. Therefore, the ANOVA results indicate for the framework Si/Al ratio, the main influential factors are the amount of additional silica sources(A) and alkali(B), and their contribution percentages(p) are 44.83% and 44.15%, respectively. As for the relative crystallinity, the amount of additional silica sources, alkali, and crystallization time have contribution percentage of 42.46%, 30.88% and 24.88%, respectively.

The NaY sample with high Si/Al ratio(5.5) and relative crystallinity(88.3%) was synthesized at the optimal conditions. Its Si/Al ratio and relative crystallinity are in good agreement with those predicted by Taguchi method. The prepared zeolite possesses uniform particle size, large surface area and narrow pore size distribution.

References:

[1] Wang Y C, Shen B J, Zeng P H. *Petro. Sci*., **2005**,**2**:57~61

[2] Chandrasekhar S, Pramada P N. *Appl. Clay Sci.*, **2004**,**27**: 187~198

[3] Elliott C H, J Baltimore, et al. *U.S. Patent* 3,639,099, **1972.**

[4] Liu H H, Zhao H J, Gao X H, et al. *Catal. Today*, **2007**,**125**: 163~164

[5] Wang B, Ma H Z. *Microporous Mesoporous Mater*., **1998**,**25**: 131~136

[6] LIU Xin-Mei(刘欣梅), QIAN Ling(钱 岭), YAN Zi-Feng(阎子峰). *J. Petrochem. Univ.* (*Shiyou Huagong Gaodeng Xuexiao Xuebao*), **1997**,**10**(4):26~30

[7] Liu X M, Yan Z F. *Catal. Today*, **2001**,**68**:145~147

[8] Liu X M, Yan Z F. *Acta Chimica Sinica*, **2000**,**58**(8):1009~10011

[9] Dight L B, Annandale, Bogert D C, et al. *U.S. Patent* 5,023,220, **1990.**

[10]Brown S M, Plains S, Woltermann G M, et al. *U.S. Patent* 4,235,753, **1980.**

[11]Ding L H, Zheng Y, Hong Y, et al. *Microporous Mesoporous Mater*., **2007**,**101**:432~439

[12]Liu W L, Hsieh S H, Chen W J, et al. *Surface Coatings Technol.*, **2007**,**201**:9238~9242

[13]Anawa E M, Olabi A G. Optics Laser Technol., **2008**,**40**:379~388

[14]Madaeni S S, Koocheki S. *Chem. Engin. J*., **2006**,**119**:37~44

[15]Basavarajappa S, Chandramohan G, Davim P J. *Mater. Design*, **2007**,**28**:1393~1398

[16]Taguchi G. *Taguchi on Robust Technology Development Methods*, New York, NY: ASME, **1993**.1~40.

[17]Ch en D C, Chen C F. *J. Mater. Proc. Technol*., **2007**,**190**: 130~137

[18]Kin K D, Choi D W, Choa Y H, et al. *Colloids Surfaces A*: *Physicochem. Eng. Aspects*, **2007**,**311**:170~173

[19]Bhardwaj S, Sharon M, Ishihara T. *Current Appl. Phys*., **2008**, **8**:71~77

[20]Özdemir C, Akın A N, Yıldırım R. *Appl. Catal. A*: *General*, **2004**,**258**:145~152