Influence of Reaction Conditions on the Crystal Size and Yield in Hydrothermal Synthesis of ZSM-5 Molecular Sieve Zeolites

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Abstract. Nanocrystalline ZSM-5 can be used as catalysts or catalyst supports, and it has higher catalytic efficiency compared with micro-sized ZSM-5 zeolite because of its large specific surface area, so it attracted wide attention. This paper mainly discusses the hydrothermal synthesis of nanocrystalline ZSM-5.Aluminium nitrate, tetrapropyl ammonium hydroxide(TPAOH) and tetraethyl orthosilicate(TEOS) are used as main reactants and reaction conditions are studied such as Si/Al, dispersion medium(water, ethanol and butanol),reaction temperature and reaction time so as to probe how they affect the size and yield of product. The best reaction conditions are confirmed by experiments and ZSM-5 zeolite has a average size of 60nm and yield over 90% prepared with ethanol as dispersion medium at 100℃for 48 hours. This study lays foundation for next-step preparation of the catalyst.

Introduction

Zeolites are microporous, aluminosilicate minerals commonly used as commercial adsorbents and catalysts. The term zeolite was originally coined in 1756 by Swedish mineralogist Axel Fredrik Cronstedt and they are widely used in Ion exchange, adsorption, separation, catalyst and cracking[1-4] .Artificial zeolite has Higher purity and its structure is more stable than natural zeolite, and its Si/Al ratio can be controlled by the amount of reactant, so the study of synthetic methods is a important issue in the research of zeolite[5,6].The methods are divided into two types and the classification is weather a template is used in the method or not[7].

ZSM-5 is an aluminosilicate zeolite belonging to the pentasil family of zeolites. Patented by Mobil Oil Company in 1975, it is widely used in the petroleum industry as a heterogeneous catalyst for hydrocarbon isomerization reactions. Nanocrystalline ZSM-5 has larger specific surface area, higher surface energy, shorter porthole, better resistance to carbon deposition and sulfur poisoning compared with general size ZSM-5[8].So the it has greater research value and practical significance to study how to synthesize Nanocrystalline ZSM-5.

Reagents

The reagents used in catalyst preparation are shown in Table 1.

Tab.1. Reagents

Number	Reagent name	Purity	Manufacturer
1	Tetrapropyl ammonium hydroxide(TPAOH,40% w/w)	RG	Adamas
2	Tetraethyl orthosilicate（TEOS）	AR	Greagent
3	Aluminium nitrate($Al(NO)_3 \cdot 9H_2O$)	AR	Greagent
4	Ethanol（C_2H_5OH）	AR	Greagent
5	Butanol（C_4H_9OH）	AR	Greagent
6	Distilled water（H_2O）	-	-

Equipments

Equipments used in catalyst preparation and analysis are shown in Table 2.

Tab.2. Equipments

Number	Equipment	Model	Manufacturer
1	Precision electronic autobalance	ML-T	Mettler Toledo
2	Magnetic stirring apparatus	SZCL-A	ChangCheng
3	Vacuum drying oven	DZF-6020	JingHong
4	Muffle furnace	SK2-4-10	YiFeng Shanghai
5	Agate mortar	-	-
6	Scanning electron microscope	S-3400N	Hitachi Naka
7	X-Ray Diffractomer	X/Pert Pro 3040/60	PANalytical

Sample Preparation

The aluminum source (1000μmol of Al) was added to a 40 wt.% aqueous solution of tetrapropyl ammonium hydroxide (TPAOH,10g),then the dispersion medium(10g)was put into the mixture. Next the mixture was stirred vigorously under a low temperature(0-10℃) until it was pure and transparent. Then the tetraethyl orthosilicate (TEOS) was slowly dropped into the mixture(1mL/min) while stirred and the weight of TEOS was calculated by the Si/Al ratio. And then the mixture was moved to room temperature for a period of time and stirring was continued. After the hydrolysis of itraethyl orthosilicate (TEOS) was complete, the mixture was moved into a tetrafluoroethylene-lined hydrothermal reaction kettle and sealed, then the reactor was put in a vacuum oven for a period of time at a certain temperature. Next the reactor was opened and mixture was taken out for centrifugal, after that supernatant was abandoned and distilled water was added again to dissolve the solid substances retained for centrifugal again. This action was repeated for 3 times so as to wash away the residual reactants. Then the wet solid substance was put in vacuum oven and when it get dry it was put into a muffle furnace calcined at 540℃ for 4-8h under a nitrogen atmosphere. Last, the sample was taken out to grind in a agate mortar which is the final product of the experiment.

The sample was weighed and recorded as m_1,the quality of TEOS was converted into SiO_2 and recorded as m_2 and the quality of $Al(NO)_3 \cdot 9H_2O$ was also converted into Al_2O_3 which recorded as m_3.The yield was defined as the g of calcined solid per g of SiO_2 and Al_2O_3 in the initial mixture.

The calculation method of yield can expressed as：

$$Yield = \frac{m_1}{m_2 + m_3} \times 100\% \quad (1)$$

Analytical Method

Si/Al ratio: EDTA complex titration

Crystal-size dimension: Scanning electron microscope

Results and Discussion

Main influence factors during ZSM-5 zeolite sample preparation are studied include the dispersion medium type, hydrolysis time,hydrothermal temperature,hydrothermal time and Si/Al ratio. The samples were analyzed and the result is written below.

Hydrolysis time

In this group of experiments, distilled water was used as dispersion medium; hydrothermal temperature was 100℃ and hydrothermal time was 48h.Effect of hydrolysis time to crystal sizes and yield was studied. The data is written in Table 3.

Tab.3. Effect of hydrolysis time to crystal sizes and yield

Sample Number	Hydrolysis time(h)	Si/Al ratio	Crystal size(nm)	Yield(%)
4	12	79.8	120	78.7
1	24	80.1	80	90.1
5	48	80.2	80	93.9

As shown in Table 3, when hydrolysis time is below 24h,crystal size is larger and yield is lower, proving that reaction was not complete; when hydrolysis time is or above 24h,crystal size did not narrow any more but yield was still rising gently. After analysis several points were proposed to explain the reason.

First, vigorous stirring do good to narrow the crystal size. Nanocrystalline ZSM-5 easily become agglomeration in liquid medium and vigorous stirring make rate of mass transfer of crystals higher which prevents nanocrystalline ZSM-5 from being agglomeration.

Secondly, magnetic stirring works as a changing electromagnetic field, interfere with the mass points from ordered.So it reduces the growth rate of crystals and promotes numerous small-size crystals in liquid medium[9].

Thirdly, many big-size crystals form in the begining of reaction while part of reactants do not participate in it. When hydrolysis time is below 24h,yield is lower; along with the prolong of stirring, big-size crystals are damaged and converted to small ones , lots of small-size crystals generate and more reactants join in the reaction, so yield rise and crystal size reduce when stirring time been prolonged.

Hydrothermal temperature

In this group of experiments, distilled water was used as dispersion medium; hydrolysis time was 24h and hydrothermal time was 48h.Effect of hydrolysis time to crystal sizes and yield was studied. The data is written in Table 4.

Tab.4. Effect of hydrothermal temperature to crystal sizes and yield

Sample Number	Hydrothermal temperature(℃)	Si/Al ratio	Crystal size(nm)	Yield(%)
1	100	80.1	80	90.1
6	120	82.3	140	93.5
7	140	80.3	300	96.1

As shown in Table 3.2,when hydrothermal temperature rise in the range of 100 to 140℃,crystal size rise sharply and yield rise gently. After analysis several points were proposed to explain the reason.

First, higher-temperature environment makes reaction faster and higher pressure in reactor, which are beneficial to form big-size crystals of ZSM-5.

Secondly, lower-temperature environment makes reaction slower and lower pressure in reactor, which delay the form of big-size crystals of ZSM-5,and small ones remains more.

Hydrothermal time

In this group of experiments, distilled water was used as dispersion medium; hydrothermal temperature was 100℃ and hydrolysis time was 24h.Effect of hydrothermal time to crystal sizes and yield was studied. The data is written in Table 5.

Tab.5. Effect of hydrothermal time to crystal sizes and yield

Sample Number	Hydrothermal time(h)	Si/Al ratio	Crystal size(nm)	Yield(%)
8	24	80.6	80	62.5
1	48	80.1	80	90.1
9	72	80.3	80	96.4

As shown in Table 3.3, hydrothermal time affect little to crystal size. When hydrothermal time is below 48h, yield is affected seriously; when hydrothermal time is or above 48h, yield is affected little, too.

Si/Al ratio

In this group of experiments, distilled water was used as dispersion medium; hydrothermal temperature was 100℃;hydrolysis time was 24h and hydrothermal time was 48h.Effect of Si/Al ratio to crystal sizes and yield was studied. The data is written in Table 6.

Tab.6. Effect of Si/Al ratio to crystal sizes and yield

Sample Number	Si/Al ratio	Crystal size(nm)	Yield(%)
10	39.7	80	90.8
1	80.1	80	90.1
11	120.7	80	91.5
12	160.4	80	90.3

As shown in Table 6,when Si/Al ratio is adjusted by changing the amount of reactant, crystal size change little and yield is quite stable. It proves that there is no relevance between Si/Al ratio and samples' crystal sizes and yield. In some of other synthesis methods, aluminum atoms are more difficult to enter zeolite structure so the Si/Al ratio rise[10-12].And in non-template methods, the Si/Al ratio is always lower than template methods[13].

Dispersion medium

In this group of experiments; hydrothermal temperature was 100℃; hydrolysis time was 24h and hydrothermal time was 48h.Effect of dispersion medium to crystal sizes and yield was studied. The data is written in Table 7.

Tab.7. Effect of dispersion medium to crystal sizes and yield

Sample Number	Dispersion medium	Si/Al ratio	Crystal size(nm)	Yield(%)
1	Distilled water	80.1	80	90.1
2	Ethanol	81.3	60	91.2
3	Butanol	79.5	60	90.7

As shown in Table 3.5,when ethanol or butanol is used to place of distilled water, crystal sizes reduce obviously and the reason is expound below(use ethanol as an example).

Frist, aqueous ethanol has a high permittivity compared to distilled water, so the electrostatic repulsion among primary particle is enlarged and particles is not easy to be aggregation.

Secondly, in the hydrothermal synthesis reaction process, ethoxy of ethanol molecules replaces the non-hydroxy skeleton bridge of micelle surface, so suction among granules reduced and the system get more dispersible.

Thirdly, ethanol also works as surfactant, which also do good to cut down the crystal size.

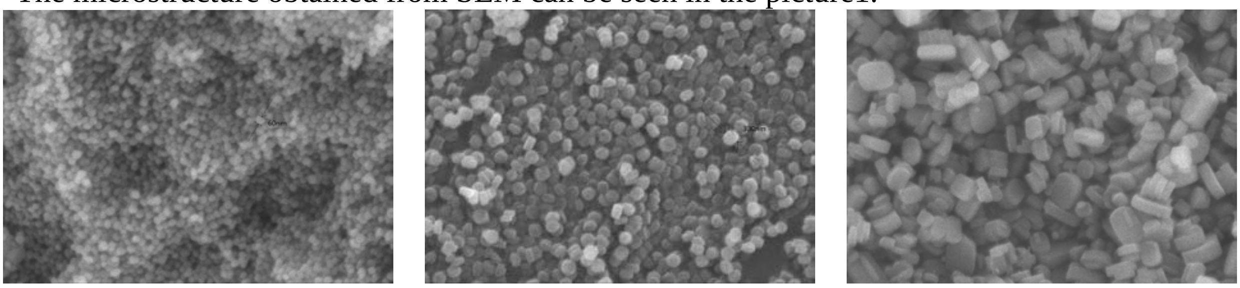
Lastly, changing of dispersion medium has no affection to extent of reaction, so it affect little to yield.

Microstructure and XRD

Sample were taken for SEM and XRD test for further analysis.

The magnification of SEM is from 10,000 to 100,000.

The microstructure obtained from SEM can be seen in the picture1.



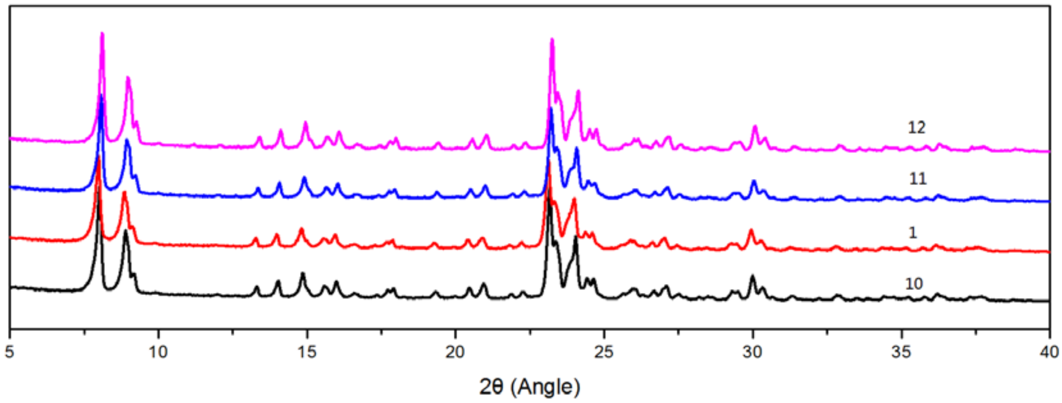
(a) Sample 2(40,000) (b) Sample 7(40,000) (c)Sample 4(100,000)

Pic.1. The microstructures of sample 2,7 and 4,with its magnification in brackets

From picture 1(a),1(b) and 1(c),conclusion can be given that No.2 sample has the smallest crystal size of 60nm while No.7 sample has the biggest crystal size of 300nm.No.4 sample has irregular shape and larger size because of the too short hydrolysis time that makes the reaction incomplete, so average size was recorded as 120nm.

In short, when hydrolysis time is not enough, reaction will be affect badly that sample has neither regular shape or small crystal size.Instead, when hydrolysis time is enough, other conditions only affect the crystal size and the crystal size is stable in single sample.

XRD scanning conditions : scanning angle is from 10-40° and scanning speed is 5°/min.



Pic.2. The XRD of Sample 12,11,1 and 10

Picture 2 shows that the two highest peak are both typical MFI zeolite diffraction peaks, and the samples have high degree of crystallinity. The four samples’ crystal sizes are approximative judging by the peak width from XRD graph, which meets the solution from SEM pictures. It proves that Si/Al ratio affect little to crystal size.

Conclusion

Nanocrystalline ZSM-5 samples were synthesized by hydrothermal crystallization and the conclusion is written below:

(1)In these reaction conditions, the dispersion medium type,hydrolysis time and hydrothermal temperature obviously affect the crystal sizes while hydrothermal time and Si/Al ratio affect the crystal sizes very little.

(2)When ethanol or butanol was used as dispersion medium, the crystal sizes of ZSM-5 was 60nm,which was much better than distilled water.

(3)The best reaction conditions was defined that ethanol or butanol is used as dispersion medium; stirring time of the mixture is 24h;hydrothermal temperature is 100℃;hydrothermal time is 48h.

(4)XRD shows that the samples have a high degree of crystallinity.

(5)When yield is below 90% the reaction is incomplete. The samples’ crystal sizes is larger than normal and its surface microtopography looks irregular. To prolong the hydrothermal time will effectively solve the problem.

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