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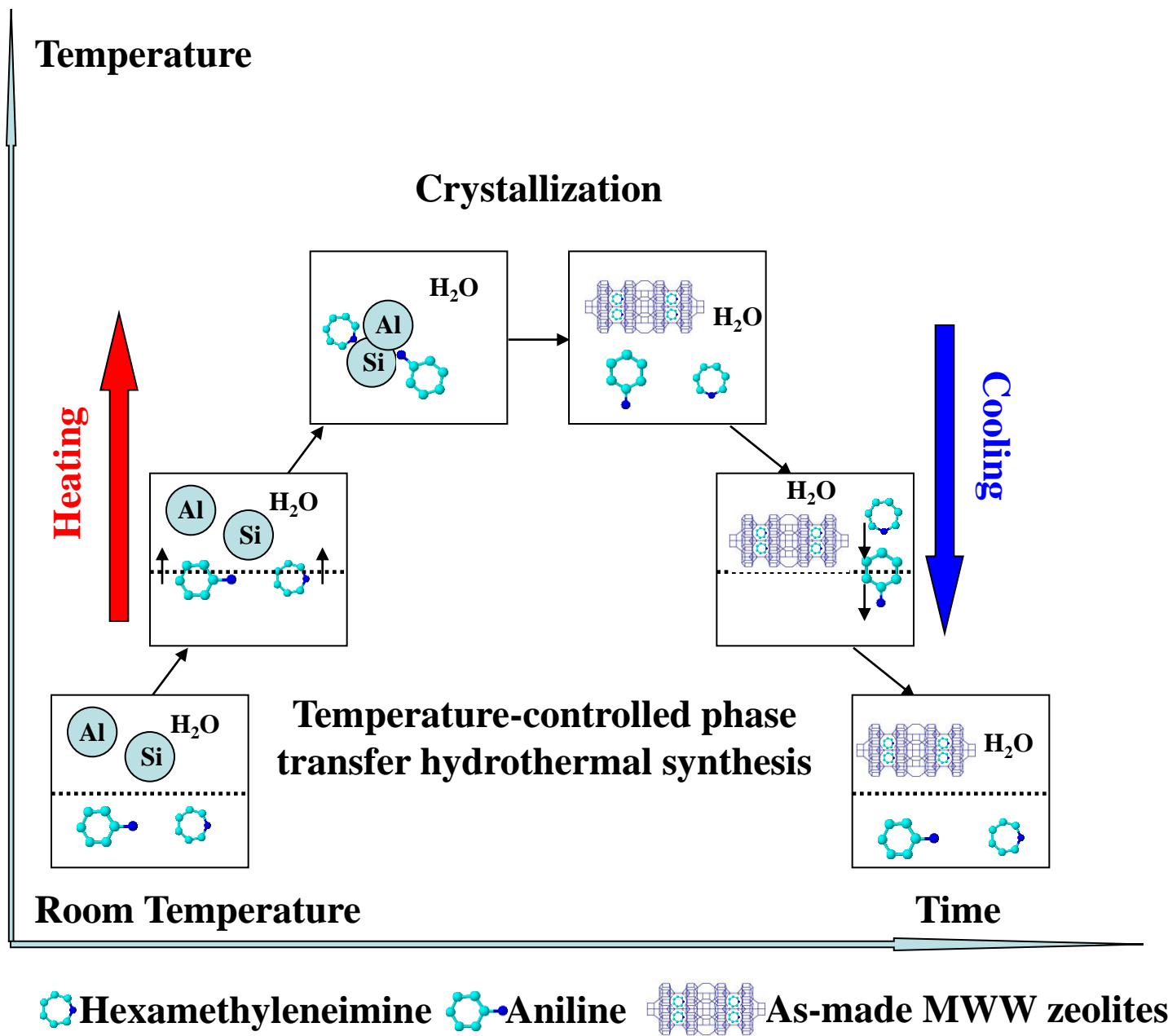


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COMMUNICATION

Temperature-controlled phase transfer hydrothermal synthesis of MWW Zeolites

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Temperature-controlled phase transfer hydrothermal synthesis of MWW zeolites was realized with hexamethyleneimine as structure-directing agent and aniline as structure-promoting agent. During crystallization, hexamethyleneimine and aniline were completely soluble. After crystallization with temperature decreased, aniline extracted hexamethyleneimine from mother liquid to organic phase for reuse.

Introduction

MCM-22 zeolite (International Zeolite Association: IZA code MWW), firstly synthesized by Mobil researchers, represents an original zeolite with the combination of two classes of materials: zeolites and layered solids, which have two independent pore systems: two-dimensional, sinusoidal, ten-ring intralayer channels and 12-ring interlayer supercages, both accessible through ten-ring apertures^{1,2}. There is a family of materials with a structure related to MWW, such as MCM-22, MCM-56, and MCM-49, where the differences between them are mainly due to the packing degree of the layers; MCM-49³ presents the same framework topology as calcined MCM-22, and MCM-56⁴ maintains the single-layered structure on calcination. Related materials are the aluminosilicates SSZ-25, the boron-containing analog ERB-1, and the pure silica polymorph ITQ-1. MWW zeolites were usually synthesized by the utilization of cyclic amines and organic cations as templates. For aluminosilicates MWW zeolites (MCM-22, MCM-49, MCM-56 and SSZ-25) hexamethyleneimine (HMI) is the most usually used template. Severe toxicity and difficulty in recovery of HMI are the major challenges for the hydrothermal synthesis of MWW zeolites.

For most scientists and engineers in chemistry, there are two common challenges to be solved. One is the separation homogenous catalysts from reaction mediums; the other is the poor diffusion capability of reactants and products on heterogeneous catalysts. To overcome this contradictory issue, the concept of thermal-regulated phase transfer was raised⁵⁻⁹: thermal-regulated phase transfer

catalysis and thermal-regulated phase-separable catalysis. Another phase transfer application was the reaction controlled phase transfer catalysis for propylene epoxidation to propylene oxide¹⁰. All of above mentioned phase transfer catalysis is featured by the combined merits of high activity of homogenous catalysis and the easier separation of catalysts from products as in heterogeneous catalysis in one catalytic process.

As summarized above, the hydrothermal synthesis of MWW zeolites seems to have the same problems. Can the concept of phase transfer be applied in conventional hydrothermal synthesis? It seems that the involvements of phosphines, polyethylene glycol and $P[C_6H_5-O-(CH_2CH_2O)_nH]_3$ into hydrothermal synthesis are a troublemaker rather than an improver. Are there simple methods to achieve the phase transfer in the hydrothermal synthesis? Since the hydrothermal synthesis is temperature sensitive, much effort has been devoted to find the organics with positive temperature-dependent solubility. It is well known that phenol and aniline are featured by improved solubility in water with the increase of temperature. As for zeolite synthesis, obviously aniline is more favourable choice than phenol. Interestingly, there are almost no published results about the zeolite synthesis with aniline as template, which reminds us not to use aniline as template. To overcome this problem, co-template methodology is adopted. As well known, co-template methodology was extensively investigated and reviewed all over the world^{11,12} for the sake of lowering the cost and toxicity of zeolite synthesis. What may be the first example of this synthesis strategy was provided by Mobil researchers who reported the crystallization of zeolites ZSM-39 and ZSM-48 from gels containing tetramethylammonium cations and propylamine¹³⁻¹⁵ in 1980. One type of co-template strategy developed by Universal Oil Products (UOP) is called charge density mismatch (CDM)¹⁶, by which the zeolites UZM-4 and UZM-5 with two open-frameworks were synthesized from tetramethylammonium ions/tetraethylammonium ions mixed systems¹⁷. In chevron, Zones and Hwang^{11, 18} have developed a co-template approach for the

preparation of zeolites using multi-organic amines instead of expensive organic templates, for example, a cheap isobutylamine together with a small amount of aminoadamantane to template SSZ-25 (MWW). Furthermore, a series of zeolites such as SSZ-13 (IZA code CHA), SSZ-33 (IZA code CON), SSZ-35 (IZA code STF), and SSZ-42 (IZA code IFR) have also been prepared in the same manner by the same group¹⁹. Although co-template strategy was extensively investigated, MWW structure zeolite is one of the mostly synthesized examples from co-templates, for example SSZ-25 directed by, N, N, N-trimethyl-1-adamantanammonium(TMAAd⁺)/isobutylamine, TMAAd⁺/piperidine and polycyclic amines/isobutylamine²⁰, ITQ-1 by TMAAd⁺/dipropylamine, and TMAAd⁺/hexamethyleneimine²¹, MCM-22/49 by HMI/cyclohexylamine co-templates²². Therefore, aniline is selected to be one of the co-templates used for MWW zeolite synthesis. Even till now, the lack of published results about aniline as template has always confused us. To our best knowledge, three Chinese patents were found about the use of aniline as co-template, the ideas of which originated from CN 1565968A. In this patent, the selection of co-templates covered almost all potential templates, such as hydrocarbons, organic amines, alcohols, ketones. It's of great pity that the inventors did not recognize the concept of the temperature-controlled phase transfer hydrothermal synthesis.

In this paper, aniline was selected with HMI to achieve the temperature-controlled phase transfer hydrothermal synthesis of MWW zeolites. The specific role of aniline was also revealed.

Experimental

Samples of MCM-22 and MCM-49 were produced in accordance with procedures outlined elsewhere^{1, 3}. All materials (silica gel, NaAlO₂, NaOH, HMI, aniline and water) were used as purchased. The typical batch composition in terms of molar ratio was: SiO₂/Al₂O₃=30, NaOH/SiO₂=0.18, R/SiO₂=0.30, H₂O/SiO₂=15, if without specific description. The hydrothermal synthesis was carried out for 72h in a Teflon-lined autoclave under rotating condition at 145°C. The products were filtrated, washed with water, and dried at 105°C overnight. Samples were calcined at 550°C in ambient air for 10 h in a muffle furnace to remove organics. After crystallization, the organic phase was recovered by simple liquid separation for reuse. The HMI in mother liquid was eliminated by simple distillation. The distilled liquid was cooled down and collected for liquid separation to recover the organics.

X-ray diffraction (XRD) patterns of samples were collected on a D/MAX-III X-ray diffractometer (Rigaku Corporation, Japan) with filtered Cu K α radiation. ¹³C cross-polarization magic angle spinning nuclear magnetic resonance (CP/MAS NMR) experiments were performed on a Bruker AVANCE III 600WB spectrometer at a resonance frequency of 150.9 MHz using a 4 mm double-resonance MAS probe at a sample spinning rate of 7.5 kHz. The chemical shift of ¹³C was determined using a solid external reference, hexamethylbenzene. ¹³C CP/MAS NMR spectra were recorded by using a recycle delay of 5 s and a contact time of 2 ms. The liquid ¹³C NMR experiments were performed on a Varian INOVE 500 spectrometer at a resonance frequency of 125.6 MHz using a 5 mm double-resonance probe. The chemical shift of ¹³C was referenced to tetramethylsilane. ¹³C NMR spectra were recorded by

small-flip angle technique using a pulse length of 3.2 μ s($\pi/6$) and a recycle delay of 4 s.

Results and discussions

Temperature-controlled phase transfer hydrothermal synthesis with HMI/AN template

As shown in Fig. 1, the sample synthesized with HMI/AN as templates shows almost same XRD patterns as the sample with HMI as template, which confirms the successful synthesis of MWW zeolite with aniline as co-template. Different SiO₂/Al₂O₃ ratios at 30 and 20 led to the formation of MCM-22 and MCM-49 respectively, which was in accordance with the results of hydrothermal synthesis with HMI as template.

At sol-gel state, there was obvious phase separation between organic templates and mother liquid, which didn't occur in HMI system because HMI (solubility in water 17g/100g) is complete soluble in mother liquid at room temperature with HMI/SiO₂=0.30 and H₂O/SiO₂=15. As reported by Xu's group, the involvement of cyclohexylamine(CHA) in HMI/CHA systems might have several drawbacks. The poor solubility of cyclohexylamine surely had negative effects on the crystallization because of external diffusion, which showed the phenomenon that the relative crystallinity increased with the stirring speed²³. Is it the same for HMI/AN systems? The answer is definitely "no". Table 1 shows the solubility data of aniline in water. Temperature at 110°C is high enough to make aniline completely soluble in mother liquid with AN/SiO₂=0.20 and H₂O/SiO₂=15. After crystallization, with the decrease of temperature, the aniline was separated from mother liquid and zeolite to form organic phase. Simultaneously, HMI was extracted from mother liquid and zeolite except those incorporated in zeolite. In such a way, organic templates can be recovered by phase separation and simple liquid separation for reuse. In one word, the use of aniline as co-template leads to the temperature-controlled phase transfer hydrothermal synthesis without any negative effects, which provides a greener route to the synthesis of MWW zeolite.

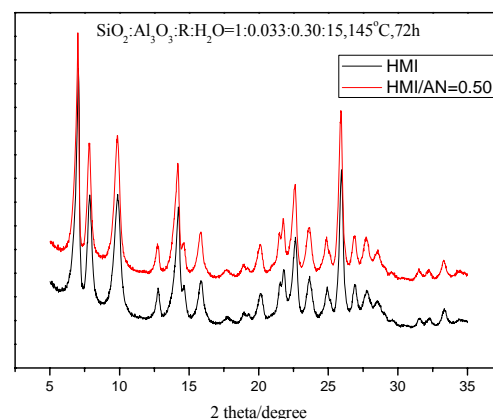


Fig.1 XRD patterns of calcined samples directed by HMI and HMI/AN

Table 1 solubility data of aniline in water²⁴

AN wt%	H ₂ O wt%	T/°C	AN wt%	H ₂ O wt%	T/°C
3.61	96.39	13.8	9.10	90.90	120
3.70	96.30	30	11.20	88.80	130
4.20	95.80	50	13.50	86.50	140
5.00	95.00	70	17.10	82.90	150
6.40	93.60	90	22.00	78.00	160
8.00	92.00	110	26.10	73.90	163

* complete miscibility with water at temperature above 167°C

Several blank experiments were performed to testify the necessity of aniline. As shown in Fig. 2a, the HMI and HMI/AN systems show similar crystallization curves until the complete crystallization at 72h. With R/SiO₂=0.30, prolonged time leads to thermodynamics-induced phase transformation from MWW to FER (IZA code) for HMI system, while not obvious for HMI/AN systems until 96h. With HMI/SiO₂=0.10 and no involvement of aniline, the relative crystallinity decreased remarkably, which confirm the necessity of aniline as co-temple to promote crystallization.

Since the MWW zeolites were successfully synthesized with HMI/AN as co-templates, aniline should be used as much as possible because of its low cost and toxicity. With R/SiO₂=0.30, the minimal amount of HMI was investigated (Fig. 2b and Table 2). It was clearly shown that aniline could only take parts of roles for the synthesis of MWW zeolites, which approved the key template effects of HMI. The similar results were also reported that HMI plays a structure-directing role, and that cyclohexylamine stabilized the framework of MWW zeolites in HMI/CHA systems²³. As shown in Table 2, the loss of crystallinity caused by low HMI/AN ratio could partially be compensated by higher crystallization temperature. Although higher temperature favours the formation of more stable phase ZSM-35, aniline as co-temple is proved to be beneficial to delay the transformation to ZSM-35. What should be noticed is that aniline cannot prevent the formation of ZSM-35, but delay the formation of ZSM-35, that is, ZSM-35 could be generated in HMI/AN systems with enough time. As for HMI/CHA systems, the crystallization should be carefully controlled to avoid the formation of ZSM-35 because cyclohexylamine is one of templates used for ZSM-35 synthesis. That's the reason why HMI/CHA co-templates is more suitable to the formation of MCM-49/ZSM-35 zeolite composites rather than MWW zeolite²⁵.

Table 2 the effects of HMI/AN ratio and temperature

T/°C	HMI/AN	t/h	Rc/%	phase
145	0.2	72	35	MCM-22
145	0.2	96	40	MCM-22
145	0.5	72	110	MCM-22
155	0.2	96	95	MCM-22
155	∞	96		ZSM-35

From above results, it is proved that aniline act as co-temple to promote the crystallisation of MWW zeolites with temperature-controlled phase transfer hydrothermal synthesis as unexpected luckiness.

Aniline as template

To further clarify the effects of aniline, the synthesis was performed with sufficient alkalinity and time to obtain crystalline phase (Table

3). Higher alkalinity (Na/SiO₂=0.50) led to the formation of MOR (Mordenite, IZA code MOR), while lower alkalinity (Na/SiO₂=0.30) to ZSM-5 (IZA code MFI). Both MOR and ZSM-5 can be synthesized without organic templates, that is, Na⁺ can direct the formation of MOR and ZSM-5. The p-π conjugation of aniline leads to low electronegativity, which surely decrease the capability of the interactions between aniline and zeolitic framework, which is to gild the lily in the MOR and ZSM-5 synthesis with aniline as sole-temple. Maybe that is also the reason why almost no published results about the hydrothermal synthesis with aniline as sole-temple. As revealed, poor structure-directing capabilities of aniline lead to the failure of MWW zeolites synthesis by itself. However, it could be expected to maintain pure phase of MWW zeolites with aniline as co-temple. For example, HMI/CHA systems, ZSM-35 is favoured by the cyclohexylamine addition, while for HMI/AN systems, aniline decrease the usage of HMI to delay the transformation from MWW to FER. Competing phase of MOR and ZSM-5 are caused by Na⁺ or misappropriate Si/Al, rather than aniline.

Table.3 aniline as the template

T/°C	NaOH/SiO ₂	t/h	phase
145	0.18	72	amorphous
145	0.30	72	ZSM-5
150	0.50	120	MOR

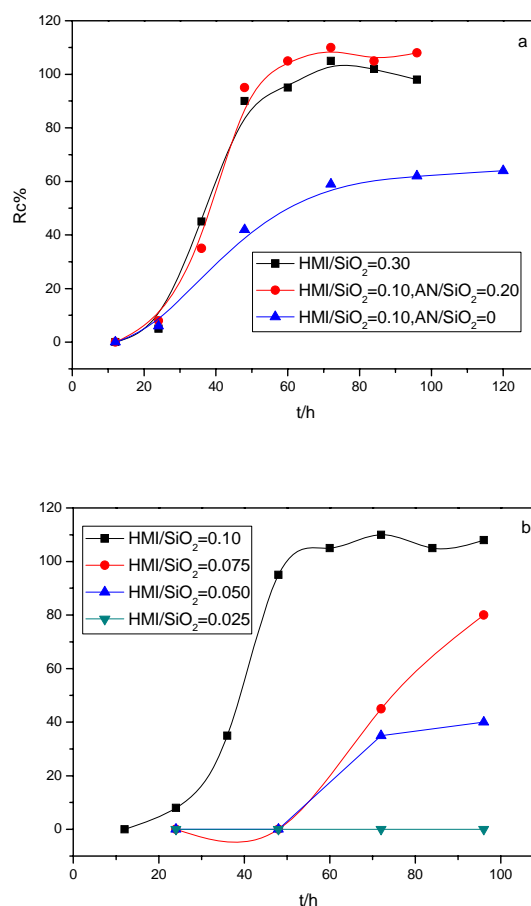


Fig. 2 the effects of HMI and AN on crystallization curves

Different templates different roles

Although in most of the experimental approaches in this field, just only one type of organic molecule is present in the synthesis gel as structure-directing agents, there are also a number of structures that require the simultaneous presence of at least two different templates to crystallize, so does in the synthesis of MWW zeolites. Davis classified templates into three different types: true templates, structure-directing agents and space-filling species^{26, 27}. Obviously HMI and aniline seem to have different roles in the synthesis. The ¹³C CP/MAS NMR of as-made samples were investigated to provide the information of HMI and aniline (Fig. 3) with the ¹³C NMR spectra of protonated/unprotonated HMI and aniline in water (Fig. 4). The HMI sample gives two C1 resonances at 49 and 57 ppm and one C2/C3 resonance at 26 ppm for the incorporated HMI molecules. In accordance with other's results, the two C1 resonances at 49 and 57 ppm in as-made MWW zeolites are associated to HMI molecules residing in interlayer and intralayer void spaces respectively^{21, 28}, but specific functions of HMI in two different spaces cannot be determined.

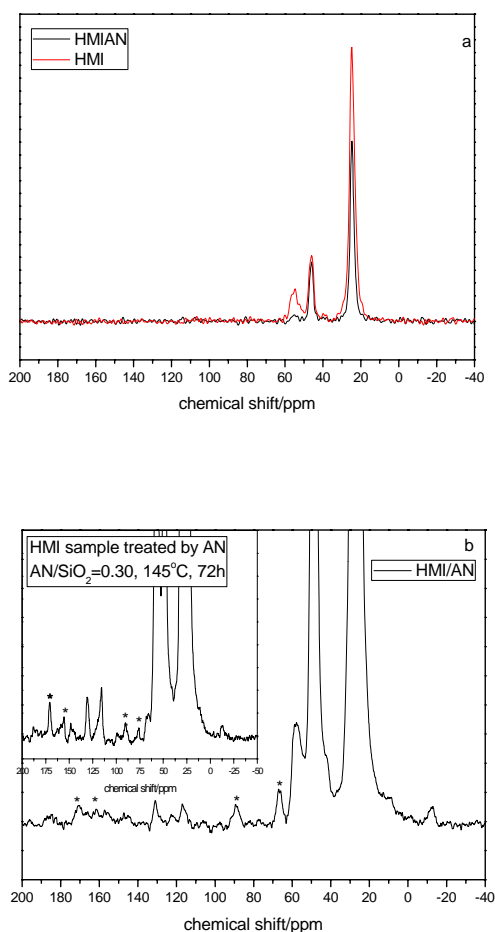


Fig. 3 ¹³C CP/MAS NMR spectra of as-made samples

For HMI/AN sample, the C1 resonance at 49 ppm is retained, while the C1 resonance at 57 ppm remarkably decreases, which also leads to the slight decrease of C2/C3 resonance at 26 ppm. The obvious decrease of C1 resonance at 57 ppm is surely caused by the chemical

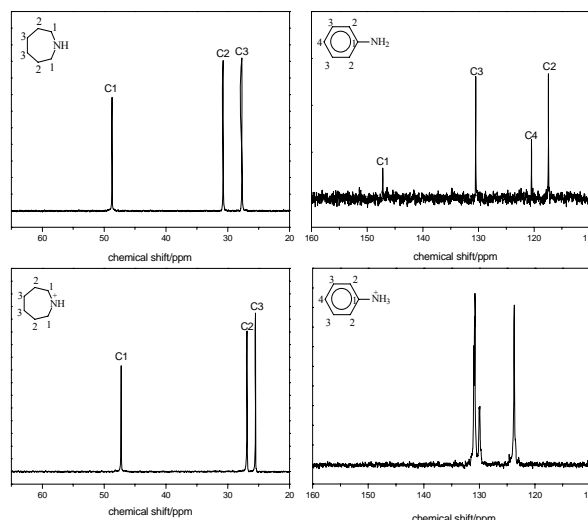


Fig. 4 ¹³C NMR spectra of HMI, AN, protonated HMI and protonated AN in water

interaction of aniline, That is, aniline takes the role of some HMI (C1 resonance at 57ppm) to promote the crystallization. Interestingly, it's really a pity that no resonances of incorporated aniline were detected by ¹³C CP/MAS NMR. In order to verify the incorporated aniline, so another ¹³C CP/MAS NMR was performed as long as possible to detect the resonances of incorporated aniline (Fig. 3b). Fortunately, the four very weak resonances at 100~160ppm were detected, which is in accordance with the results of unprotonated aniline in water. The existence of peaks at 100~160ppm were also detected for the HMI sample treated by aniline. It's unprotonated aniline that takes the role of unprotonated HMI (C1 resonance at 57ppm) to promote the crystallization of MWW zeolites. However the amount of aniline incorporated into zeolites seems almost to be neglected. As shown in Fig. 3b, the ¹³C resonances of incorporated aniline were too weak to be detected. The structure-promoting effects of aniline proved by hydrothermal synthesis and the remarkable decrease of C1 resonance at 57ppm are contradictory with the almost no detections of incorporated aniline. To our best knowledge, the similar phenomenon was encountered by UOP researchers in 1989. It was proved that tetraethylammonium hydroxide and tripropylamine co-directed the formation of AlPO₄-52 but almost little tripropylamine was found in as-made zeolite^{29, 30}. Xu et al³¹ suggested that it is maybe too complicated to be explained. As for HMI/AN template, a hypothesis is suggested. During crystallization at higher temperature, aniline does have chemical interaction with zeolite components (Si, Al and HMI). While with the decrease of the temperature after crystallization, the aniline is moved out of zeolitic frameworks. The driving force is assumed to be the dramatic change of the interaction between aniline and H₂O caused by temperature, which accounts for temperature sensitive solubility of aniline. With the decrease of temperature, driving force for phase separation can move the incorporated aniline out of the zeolites into organic phase. In such a case, only unprotonated aniline could be moved, because protonated aniline must be replaced by other protonated species. The four very weak resonances of aniline were also proved to be that of unprotonated aniline. At present, this

hypothesis seems too hard to be proved. Many efforts have been made but with little improvements, which need more focus on it.

From above, several conclusions can be drawn: (1) the C1 resonance at 49 ppm is associated to the structure-directing HMI; (2) the C1 resonance at 57 ppm of HMI is associated the pore-filling HMI; (3) unprotonated aniline can take the place of pore-filling HMI (C1 resonance at 57 ppm, unprotonated) to promote the crystallization; (4) aniline cannot take the place of structure-directing HMI (C1 resonance at 49 ppm).

On the whole, aniline acts as structure-promoting agent to promote the crystallization. The almost no consumption of aniline provides an economic and greener way of MWW zeolite synthesis. With regarding the temperature-controlled phase transfer hydrothermal synthesis as a catalytic process, the aniline is "catalysis" to the hydrothermal synthesis of MWW zeolite. During crystallization, aniline reacts with other zeolite components (Si, Al and HMI) to form transition-state. While after crystallization, aniline was moved out of the zeolite and mother liquid to achieve phase separation.

The recovery of HMI

As described in introduction, the ideal hydrothermal synthesis should be featured by easy recovery and reuse of organic templates. After crystallization, with the decrease of temperature, the positive temperature-dependent solubility of aniline also offer an integrated process for phase separation and the extraction of HMI from as-made zeolites and mother liquid. Poor solubility of aniline at room temperature provides the simple method to recover organic templates by liquid separation, but what are the methods for HMI and aniline residing in solution after the integrated phase separation and extraction? As well known, aniline and water are featured by the minimum boiling mixtures or positive azeotropes (98.5°C, 16 wt. % AN), so is for HMI and water systems (95.5°C, 49.5 wt. % HMI). The mother liquid was distilled to eliminating HMI and aniline at low concentrations, esp. HMI, which is acute toxicity to fish. HMI (pKa=11.07) show strong alkalinity in water, while aniline (pKb=4.87) show almost no alkalinity in water. The simple distillation was performed in a flask with cooler to collected distilled liquid for reuse. The pH value of distillation liquid was characterized. The pH value of first drop was about 13. The distillation stopped until pH of tested drops became 8. The collected liquids are composed of HMI, aniline and water, and accounts for around 25% of total mother liquid. The residual liquid was subject to ¹³C NMR characterization. The results show almost no HMI in residual liquid. In order to verify the fact that there is no HMI in distilled liquid with pH<8. the collected liquid samples (pH=8) was analyzed by both ¹³C NMR and gas chromatography. Both of the results confirmed the complete elimination of HMI in mother liquid. The pH value of distilled drops decrease from 13(the first drop) to 8(the ending drop) means the at least 10⁵ gap of HMI concentration in distilled liquid, which can guarantee the complete elimination of HMI from mother liquid. As for aniline it also works with a larger amount of distilled liquid. This method can also be applied to washing water, which is featured by lower HMI concentration than mother liquid.

The complete elimination of HMI in mother liquid and washing water were nearly referred. To our great fortune, the difficulties were solved by the combination of temperature-controlled phase transfer hydrothermal synthesis and simple distillation.

The reuse of recovered templates

Since the temperature-controlled phase transfer hydrothermal synthesis provides simple and almost complete recovery of organics, esp. for HMI. The key lies in the reuse of recovered organics which is consisted of HMI, aniline and water (about 20wt. %). For simplicity, the organics was regarded as aniline, with ignorance of HMI. The aqueous phase was used as water for following synthesis. As show in Table 4, the reuse of recovered organic templates has almost no negative effects on the following synthesis.

Table.4 the reuse of recovered templates

AN/SiO ₂	HMI/SiO ₂	Rc/%	BET / m ² /g
0.20(fresh)	0.10	110	508
0.20(recovered)	0.10	110	502
0.20(recovered)*	0.10	108	510

* Recovered organics treated with NaCl for further phase separation

In HMI-only conventional recipe, the recycle of HMI was achieved by the reuse of mother liquid because HMI are completely soluble in mother liquid. However the recycle of mother liquid suffers two drawbacks. one is the accumulation of Na⁺, which could leads to the formation of MOR and ZSM-35. The other is the meta-stability of MWW zeolites seeds. Longer crystallization time and higher temperature favour the formation of ZSM-35, the thermal dynamically stable zeolite. Obviously, the reuse of organics in temperature-controlled phase transfer hydrothermal synthesis can avoid the negative effects of Na⁺ accumulation and MWW seeds.

Comparison with conventional hydrothermal synthesis

Temperature-controlled phase transfer hydrothermal synthesis of MWW zeolites are compared with conventional hydrothermal synthesis. The properties of HMI and aniline are listed in Table 5.

Table.5 the properties of HMI and AN

	HMI	AN
Cost RMB/ton	40000~50000	10000
Boiling point/°C	138	184
LD50, rat, mouse /(mg/Kg)	33	442
Solubility at 20°C/(g/100g)	17	3.60

Table.6 Detailed comparison of HMI/AN and HMI systems

	HMI	HMI ^{22,33}	HMI/AN
R/SiO ₂ ,	0.30~0.35	0.18~0.20	0.30, 0.10
HMI/SiO ₂	0.30~0.35	0.18~0.20	
Pressure/MPa	0.42~0.48	Not referred	0.32~0.37
Temperature/°C	145	Above 160	145
Time/h	72	Less than 24h	72
Cost	100 base	70~80	50 or less
Features	Conventional	Conventional	Temperature-controlled phase transfer
Competing phase	Easy to FER	Easy to FER	FER
HMI recovery	Not referred	>80%, distillation	100%, liquid separation and distillation
HMI in water	Not referred	Not referred	Complete elimination

Obviously, besides temperature-controlled phase transfer hydrothermal synthesis, the use of aniline as structure-promoting agent is of lower cost, pressure and toxicity. As for HMI/AN systems, the cost could be decreased to 50% of HMI system based upon raw materials costs without consideration of extra utility cost

and energy consumption for organics recovery. The pressure decreased from 0.42MPa to 0.33MPa. The detailed comparison between HMI/AN systems with conventional HMI system are listed in Table 6. The synthesis with HMI as template was focused on the optimization of crystallization to achieve less HMI usage and better efficiency. To our great confidence, the temperature-controlled phase transfer hydrothermal synthesis suppresses the conventional HMI system. The major disadvantage of this process is the supplementary units and energy needed for distillation and liquid separation for complete recovery of HMI, which has been seldom referred in the literature.

Conclusion

Temperature-controlled phase transfer hydrothermal synthesis can be summarized as follows: (1) Aniline is insoluble in mother liquid and HMI is extracted to aniline phase at room temperature. (2) At crystallization temperature, the aniline and HMI become soluble in mother liquid to favour crystallization. (3) After crystallization, with the decrease of temperature, aniline becomes insoluble again to achieve an integrated process of phase separation and extraction of unincorporated HMI from zeolite and mother liquid to organic phase. In HMI/AN systems, HMI is structure-directing agent. Aniline is structure-promoting agent. The involvement of aniline leads to three unexpected functions: (1) Aniline acts as structure-promoting agent to fill pore of MWW zeolites during crystallization. Little incorporated aniline is detected on the as-made zeolites; (2) Aniline is the phase transfer mediums to achieve temperature-controlled hydrothermal synthesis; (3) Aniline is the extractor to extract HMI to organic phase for the recovery of HMI and aniline.

The temperature-controlled phase transfer hydrothermal synthesis of MWW zeolites is achieved by the involvement of low toxic aniline as structure-promoting agent with HMI as structure-directing agent, which leads to easy and even complete recovery of HMI in solution. Also no incorporated aniline means no consumption and potential complete recovery of aniline in hydrothermal synthesis. The reuse of recovered organics as aniline surely decreases the cost of MWW zeolites. Low cost and almost no consumption of aniline can decrease the MWW zeolites cost by approximately 50% or more in a greener way. The hydrothermal synthesis of MWW zeolites has been successfully realized with organic templates reuse in the 1m³ demonstration units in Hunan Jianchang Petrochemical Company, Sinopec, the results of which will be reported soon. For applications of this method, we would like to investigate the structure-promoting effects of aniline with organic cations as structure-directing agents. Also great interests were focused on the potential applications of temperature-controlled phase transfer hydrothermal synthesis to not only other MWW zeolites, but also beta, ZSM-5, MOR and SAPO zeolites.

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Notes and references

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