

Expanding the synthesis field of high silica zeolites

Diandian Shi, Kok-Giap Haw, Cassandre Kouvatas, Lingxue Tang, Yiying Zhang, Qianrong Fang, Shilun Qiu, Valentin Valtchev

▶ **To cite this version:**

Diandian Shi, Kok-Giap Haw, Cassandre Kouvatas, Lingxue Tang, Yiying Zhang, et al.. Expanding the synthesis field of high silica zeolites. Angewandte Chemie International Edition, 2020, Functional Porous Materials Chemistry, 59 (44), pp.19576-19581. 10.1002/anie.202007514 . hal-02875460

HAL Id: hal-02875460

https://normandie-univ.hal.science/hal-02875460

Submitted on 14 Apr 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

HAL
archives-ouvertes.fr

Expanding the Synthesis Field of High-Silica Zeolites

Diandian Shi, Kok-Giap Haw, Cassandre Kouvatas, Lingxue Tang, Yiying Zhang, Qianrong Fang, Shilun Qiu, Valentin Valtchev

▶ **To cite this version:**

Diandian Shi, Kok-Giap Haw, Cassandre Kouvatas, Lingxue Tang, Yiying Zhang, et al.. Expanding the Synthesis Field of High-Silica Zeolites. Angewandte Chemie International Edition, Wiley-VCH Verlag, 2020, 59 (44), pp.19576-19581. 10.1002/anie.202007514 . hal-03040578

HAL Id: hal-03040578

https://hal-normandie-univ.archives-ouvertes.fr/hal-03040578

Submitted on 4 Dec 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Expanding the synthesis field of high silica zeolites

Diandian Shi,[a] Kok-Giap Haw,[a] Cassandre Kouvatas,[b] Lingxue Tang,[a] Yiying Zhang,[a] Qianrong Fang,[a] Shilun Qiu,[a] Valentin Valtchev*[b,c]

Abstract: *Aluminosilicate zeolites are synthesized under hydrothermal conditions in basic/alkaline medium in the pH range between 9 and 14. Here we report the synthesis of MFI-type zeolite in acidic medium. The critical parameter determining the zeolite formation in acidic medium was found to be the isoelectric point (IEP) of gel particles. MFI-type zeolite was synthesized above the isoelectric point of the employed silica source, where the silica species exhibit a negative charge and the paradigm of zeolite formation based on the electrostatic interaction with the positively charged template retained. No zeolite formation is observed below the isoelectric point of silica. The impact of aluminum on the zeolite formation is also studied. The results of this study will serve to extend the zeolite synthesis field of high silica zeolites to the acidic medium and thus open new opportunities to control the zeolite properties.*

Zeolites are microporous aluminosilicate molecular sieves that have a variety of significant applications in catalysis, adsorption, separation, and ion exchange.[1] The intensive industrial use of zeolites is based on their unique properties as ordered channel systems containing active sites in a well-defined confine environment, which is the origin of their unraveled shape-selectivity, and molecular sieving properties.[2]

[a] D. Shi, Dr. K.-G. Haw, L. Tang, Y. Zhang, Prof. Q. Fang, Prof. S. Qiu
State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130012, P. R. China

[b] Prof. V. Valtchev, Dr. C. Kouvatis
Normandie Univ, ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie, 6 Marechal Juin, 14050 Caen, France
E-mail: valentin.valtchev@ensicaen.fr

[c] Prof. V. Valtchev
Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, 189 Songling Road, Laoshan District, Qingdao, Shandong 266101, P. R. China

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

In general, zeolites are synthesized under hydrothermal conditions in a basic medium where the OH^- is the mineralizing agent. The conventional zeolite syntheses are performed at relatively high pH (>9) using alkali metal and/or tetraalkylammonium cation as a structure-directing agent (SDA).[3] Zeolites are also synthesized using F^- as a mineralizer. The synthesis in fluoride medium is usually performed under neutral conditions (pH = 6-8).[4] The physicochemical properties of a zeolite obtained by the hydroxide and fluoride route differ substantially.[5] Thus, both routes deserve attention, although the industrial syntheses are limited to the use of the hydroxide medium.

The synthesis in the basic medium was first developed, mimicking the zeolite formation in nature, namely the high-temperature hydrothermal conditions in pegmatites.[6] These syntheses were performed at temperatures higher than 250 °C. In the late 50ies, Milton discovered that zeolites can be obtained under much lower temperatures using highly reactive alkaline aluminosilicate hydrogels.[7] This synthesis mode, which is used in the industry, was further developed by Breck.[8]

The fluoride medium synthesis of zeolites, pioneered by Flanigen and Patton in the late 1970s,[9] was an important breakthrough diversifying the synthesis conditions and providing materials with different properties. Guth, Kessler, and co-workers further developed this synthetic route.[10] This group systematically studied the zeolite formation in fluoride medium and synthesized different microporous materials, including aluminosilicates, aluminophosphates, and gallophosphates. The syntheses were performed in the pH range 5-9, and an attempt to obtain zeolite below pH = 5 was reported.[11] However, the formation of zeolite at pH below 5 without using seeds was not achieved.

In the conventional basic/alkaline medium synthesis, the nucleation is abundant, and the crystals grow fast. Consequently, they contain a lot of intergrowths and a relatively large number

REVISED

of framework defects.[12] Under framework defects, we refer missing T (tetrahedral) atoms replaced by silanols. The presence of defect silanols has a negative impact on zeolite catalysis since it is a coke trap in the hydrocarbons conversion.[13] The silanols also decrease the hydrophobicity of the all-silica zeolitic materials.[14] Similar problems can be reduced to a considerable extent by the synthesis in fluoride medium where the crystals grow slowly, which limits the number of defects. Bleken *et al.* showed that the coke formation in ZSM-5 prepared via the fluoride route is negligible with respect to the hydroxide medium prepared counterpart.[15] Thus, the fluoride route has shown its most notable advantage in producing zeolite crystals of few framework defect sites.[16] However, the zeolite crystals synthesized in fluoride medium are usually several tens of micrometers large and impose diffusion limitations, which limits their applications. On the other side, the fluoride medium growth crystals are of great importance in fundamental studies of zeolites. From a practical point of view, the synthesis in fluoride medium might present interest since the low pH might be appropriate to incorporate transition metals in the zeolite structure.[17]

The objective of this work is to extend the zeolite formation at the pH range below 5, i.e. under acidic conditions without the assistance of seeds. This objective involves fundamental and practical aspects since the results of the study will provide valuable information about the critical factors controlling zeolite formation and bring more flexibility in the preparation of zeolitic materials with controlled properties.

It is well known that silica source plays an important role in zeolite synthesis.[18] Using different silica sources may result in changing the crystallization pathway and even in the formation of an undesired crystalline phase. The preliminary work on the optimization of gel composition and reaching a successful synthesis of the zeolite was performed with pyrogen silica known as fumed silica. We selected this silica source since it was previously used in the fluoride medium synthesis of zeolites.[10c] MFI-type zeolite was obtained from a gel with molar composition 1.0 SiO_2 : 0.5 TPABr : 0.00167 Al_2O_3 : x HF : y NH_4F : 40 H_2O, where x and y were varied to control the pH. The details on synthesis can be found in the Supporting Information. Using a gel composition with Si/Al = 300, highly crystalline MFI-type material was obtained at pH = 5.0, 3.6, and 2.3 (Figure 1). The synthesis with a gel with an initial pH of 2.3 and Si/Al = 300 was reproduced using tetraethylorthosilicate (TEOS), colloidal silica (Ludox AS-40), and silicic acid as silica sources. The pH of the mother liquor after the synthesis was measured. In all case the pH was lower than in the initial gel, but varied as a function of silica source. Thus for fumed silica, TEOS, and silicic acid the final pH was about 1.7, while for the colloidal silica 1.9. The XRD patterns of the samples synthesized from these silica sources are presented in Figure S1. Thus using fumed silica, TEOS, and Ludox AS-40 yielded pure and highly crystalline MFI-type zeolite. Only traces of MFI were observed in the synthesis with silicic acid. Poor crystallinity of zeolite phase might be due to the relatively large silica particles, which might require much longer synthesis time (Figure S2e,f). Nevertheless, this set of results proved that the crystallization of zeolitic material in acidic medium is possible. The SEM inspection showed that all silica sources yielded MFI-type crystals with the typical coffin morphology (Figure S2). The crystals range between 10 and 50 μm in size. Ludox AS-40 synthesized material contains some small particles, most probably amorphous, covering the large zeolite crystals. No traces of amorphous material were observed in the TEOS synthesized sample. The amorphous phase, large particles with random shape, dominated the product obtained with silicic acid. A few but well-shaped crystals with the characteristic of MFI-type material features were observed in this sample.

The incorporation of hetero elements in the zeolite framework is indispensable for catalytic applications, which is a major field of zeolite uses. Therefore, the impact of aluminum on the zeolite crystallization in acidic medium was studied. The best result in terms of zeolite crystallinity was obtained with fumed silica. Thus the synthesis of Al-containing MFI-type material was performed with this silica source. The crystal growth kinetics of a gel with Si/Al ratio of 300 and relatively low pH (2.3) was studied and used as a reference for the synthesis duration. The hydrothermal

treatment was performed at 160 °C. The first trace of MFI was observed after four days, and a fully crystalline material obtained after 13 days (Figure S3). This reference synthesis was used to calculate the zeolite yield, which was found to be 78 %, based on the silica plus alumina content in the initial gel. Consequently, all experiments related to the impact of aluminum on the zeolite formation under acidic conditions were performed at 160 °C for 13 days. The initial pH was 2.3 and the molar composition of the gel was 1.0 SiO_2 : 0.3 TPABr : z Al_2O_3 : 0.36572 HF : 0.17124 NH_4F : 40.6 H_2O, where z = 0.01, 0.005, 0.0033, 0.00167, and 0, giving a Si/Al ratio of 50, 100, 150, 300 and infinity (∞). The synthesized samples were denoted FS-50, FS-100, FS-150, FS-300, and FS-∞ as a function of the Si/Al ratio. The XRD patterns of the obtained products are depicted in Figure S4 and their relative crystallinity presented in Table 1.

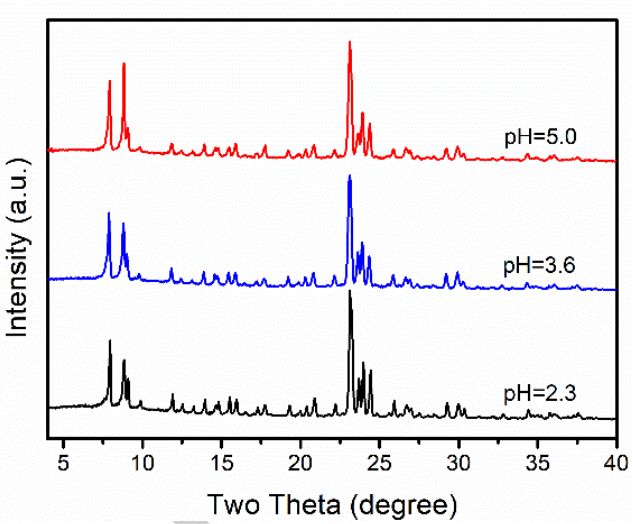


Figure 1. XRD pattern of the MFI-type samples synthesized from gels with different pH values at 160 °C for 13 days.

Table 1. Physicochemical characteristics of the MFI-type samples synthesized from gels with pH = 2.3 and different Si/Al ratios at 160 °C for 13 days using fumed silica as a silica source.

Sample	Si/Al ratio		Crystallinity	Weight loss (%)		S_{BET}	V_{micro}	V_{total}
	Initial gel	Crystalline product	(%)	25-300 (°C)	300-600 (°C)	m^2g^{-1}	cm^3g^{-1}	cm^3g^{-1}
FS-∞	∞	∞	100	0.37	12.42	336	0.18	0.18
FS-300	300	375	100	0.49	12.45	392	0.17	0.18
FS-150	150	182	100	0.88	12.34	466	0.18	0.18
FS-100	100	113	63	1.20	7.51	253	0.11	0.14
FS-50	50	61	33	3.68	5.28	128	0.05	0.12

Highly crystalline samples were obtained using gels with silicon to aluminum ratio higher than 150. The crystallinity of the samples synthesized from gels with Si/Al ratio of 100 and 50 was lower. A closer look at their XRD patterns reveals the presence of an amorphous phase, i.e., a halo in the 20-30° Two Theta range, for these two samples. The extension of the crystallization time to 18 days improved the crystallinity of FS-100 (Figure S5) and FS-50 (Figure S6); yet some amorphous material was present in the solid. The SEM inspection confirmed that FS-∞, FS-300, and FS-150 are highly crystalline products (Figure 2). The crystals are well-shaped with clean faces. No trace of other phase was observed. FS-100 and FS-50 contain crystals with the characteristic MFI-type material morphology. The crystals are covered with small particles that do not exhibit crystalline features. The amount of this phase, which we consider amorphous due to the absence of XRD pattern, is larger in the FS-50 sample (Figure S6). The results of the SEM and XRD studies are in good agreement and confirm that a high concentration of Al is not favorable for the zeolite formation in acidic medium.

The system yielding FS-300 was used to explore the pH range below 2 as the NH_4F was kept constant, and the content of HF was varied to control the pH. The formation of MFI-type zeolite was still possible at pH = 2, but the crystallinity of the sample obtained after 13 days of hydrothermal treatment was relatively low. The synthesis was extended to 18 days to get a highly crystalline product (Figure S7). Further decrease of the pH to 1.5 resulted in amorphous solid after 13 days of hydrothermal treatment. The first traces of MFI-type material were observed after 23 days of crystallization (Figure S8), while the solid obtained after 33 days contained MFI-type material and amorphous. The crystallinity of the

zeolite phase was improved after 38 days of crystallization, but new peaks in the 20 – 23° Two Theta range appeared in the XRD pattern. These peaks reveal the co-crystallization of a dense non-zeolitic phase. The synthesis at pH = 1 did not yield MFI-type material after 40 days of hydrothermal treatment.

The paradigm of zeolite formation is based on the electrostatic interactions between the positively charged templating species that remain in channels/cages of zeolite structure and negatively charged silica species that built up the framework. The surface charge of silica species

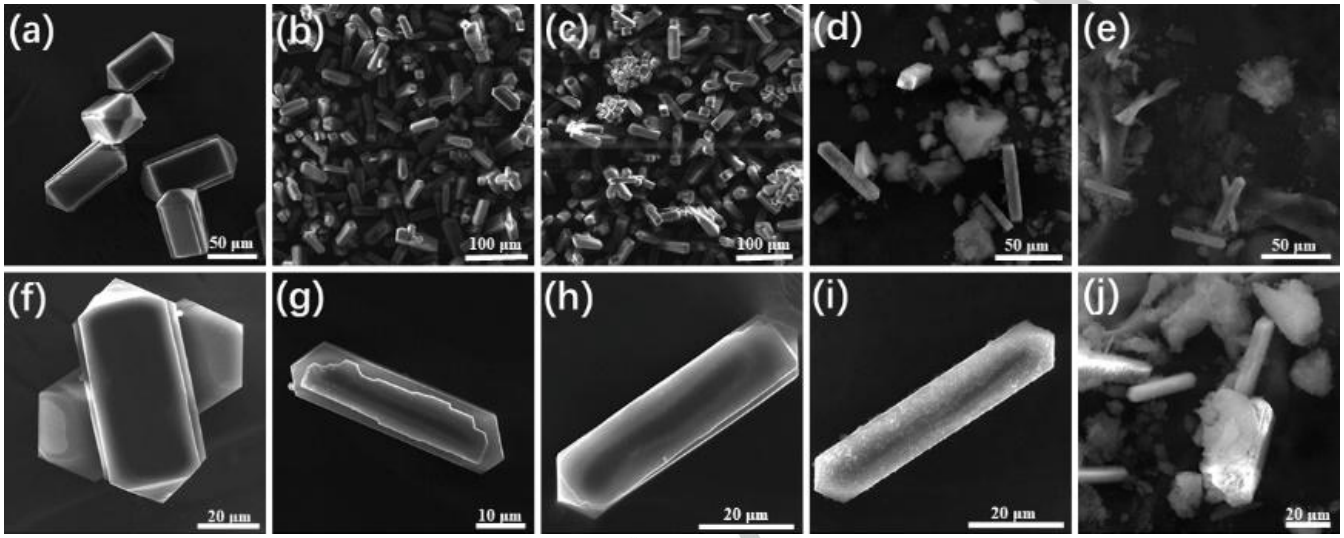


Figure 2. SEM micrographs of the MFI-type materials synthesized from gels with different Si/Al ratios at 160 °C for 13 days. Low and high magnification images of FS-∞ (a, f), FS-300 (b, g), FS-150 (c, h), FS-100 (d, i), and FS-50 (e, j).

depends on the pH of the system. Therefore, we have performed a zeta potential analysis[19] to evaluate how the pH influences the surface charge of fumed silica. The measurements were performed in the pH range 1 – 11, as each experiment was repeated ten times. Figure 3 shows the zeta potential plot of the fumed silica as a function of the pH value. The isoelectric point of the employed fumed silica, where the surface charge of silica species is electrically neutral, was found to be in the pH range 2.0 – 2.2.

The results of zeta potential measurements shed light on the crystalization behavior of MFI-type zeolite in acidic medium. The zeolite formation under acidic medium is possible solely at pH above the IEP of silica. With the decrease of the pH and approaching the IEP of fumed silica the zeolite formation is perturbed and even becomes impossible when the surface charge of silica species is inversed to positive, i.e., below the isoelectric point. In the system under investigation, we have successfully synthesized MFI-type material at pH equal to 5, 3.6 and 2.3; the latter being relatively close to the isoelectric point of fumed silica. The synthesis at a pH = 2, which is the IEP of the employed fumed silica, was still possible, but the time required to obtain a highly crystalline product was substantially extended. In the system with pH = 1.5, below but yet close to the IEP, only a part of the silica was converted into MFI-type material no matter the fact that the synthesis time was tripled. The last result might look surprising, but there is not a discrepancy in the experimental data. Namely, the surface charge in the IEP is considered neutral in the statistical mean. Close to the IEP there are still negatively charged silica species, which interact with the positively charged TPA^+. These interactions, however, are strongly perturbed, which explain the decrease in the crystal growth rate and the partial conversion of silica into the zeolite. Only when the pH of the gel is substantially below the isoelectric point, and the charge of silica is fully inverted to positive the formation of zeolite is suppressed.

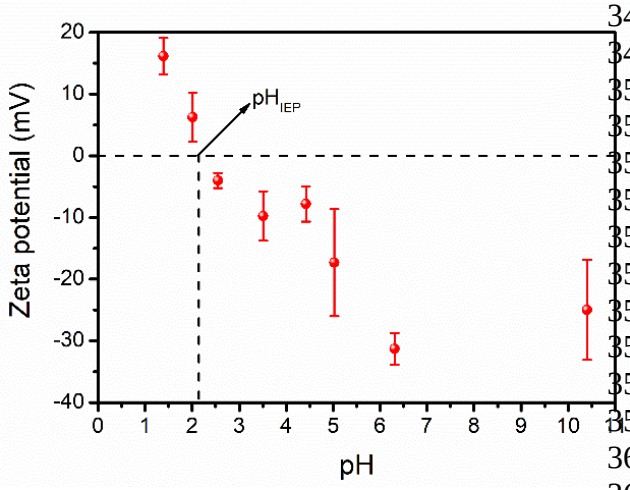


Figure 3. Zeta potential of fumed silica as a function of pH.

As reported above, the presence of Al in the initial gel has a negative impact on the zeolite formation under acidic medium. Only when Si/Al ratio is above 150, i.e., when a few Al atoms were introduced in the initial gel, the MFI-type material can be readily obtained. The crystallinity of the samples synthesized from the initial systems with Si/Al ratio of 100 and 50 was 63 and 33 % respectively (Table 1). We attribute this result to the higher IEP of aluminum hydroxide, which is at pH = 7.7.[20] Thus the positively charged aluminum species exhibit repulsive interactions with the positively charged template. Thus the zeolite formation is sensitive to the Si/Al ratio in acidic medium. This result shows that the incorporation of transition metals in the zeolite framework under acidic conditions will depend strongly on the isoelectric point of metal hydroxide.

The MFI-type materials were subjected to physicochemical characterization using complementary methods to evaluate the impact of the acidic medium on their properties. The crystallinity of materials was already discussed based on X-ray diffraction study. The short-range order was studied by comparing the ^{29}Si MAS NMR spectra of silicalite-1 synthesized in acidic medium (FS-∞), and a counterpart synthesized in basic medium (Figure S9). The resonances observed in ^{29}Si MAS NMR correspond to quaternary Qn species, with n = 1, 2, 3, or 4 stands for the number of another silicon atom directly connected to the Si atom concerned, through an oxygen bond (Si—O—Si). The two samples display resonances in the [–107 ppm; –120 ppm] corresponding to Q4 species (Figure 4). In contrast to the material synthesized in basic medium (Figure 4b), the FS-∞ sample exhibits well-resolved peaks corresponding to Q4 (Si—(OSi)4) silicon species, reflecting different crystallographic T positions in MFI-structure (Figure 4a). The Q4 resonances of the basic medium synthesized silicalite-1 (Figure 4b) are broader because of a less ordered three-dimensional Si—(OSi)4 network. Also, a broad resonance at –103 ppm corresponding to Q3 (Si—(OSi)3—OH) is observed. This is typical of a discontinuity between SiO_4 tetrahedra, leading to the formation of Si—OH bonds, and thus defect sites in the zeolite framework. However, no Q3 is observed in the spectrum of FS-∞ (Figure 4a), which is confirmed by the absence of signal enhancement in this region in the ^{29}Si{1H} CP MAS spectrum (Figure 4, inset). The last result unambiguously proves a lack of Si—OH defects in FS-∞, reinforcing the conclusion of a well-ordered 3D structure.

The FS-∞ spectrum contains a broad peak at –125 ppm, which is not observed in the reference basic medium synthesized silicalite-1. This peak is attributed to the fluoride ions, which have certain mobility between $SiO_4/2$ tetrahedra. The large signal is thus typical of framework silicon sites that undergo dynamic exchange between 4- and 5-coordinated environments, due to fluoride ion mobility.[21] Briefly, the silicalite-1 sample synthesized under acidic conditions exhibits the.

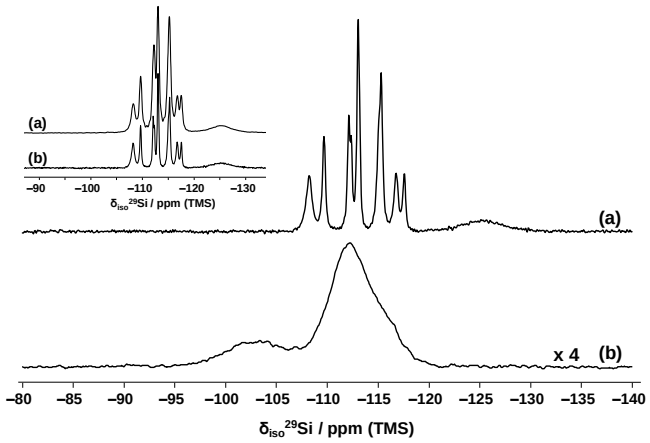


Figure 4. Weight normalized ^{29}Si MAS NMR spectra of as-synthesized silicalite-1 samples synthesized in (a) acidic (FS-∞) and (b) basic medium. Inset: (a) ^{29}Si{1H} CPMAS and (b) ^{29}Si MAS NMR spectra of as synthesized silicalite-1 samples synthesized in acidic (FS-∞) medium.

typical high ordering and absence of framework defects characteristic for the synthesis in fluoride medium

The incorporation of Al in zeolite framework was studied by ^{27}Al MAS NMR on sample FS-150. Figure S10 shows the spectra of as-synthesized and calcined ZSM-5 sample synthesized in acidic medium. Both samples exhibit aluminum signal in the region of 55 ppm corresponding to framework tetrahedral Al sites. In the case of calcined sample (Figure S10b) another resonance is observed at ≃ 0 ppm, corresponding to extraframework octahedral aluminum species, which have left the intraframework tetrahedral environment. The broadening of this signal is due to a distribution of Al^{VI} environment. The fraction of octahedral Al was ca. 10 %.

The FS series of samples were subjected to thermal analysis to evaluate template and water content (Figure S11). The weight loss below 300 °C is attributed to water release, and the one in the temperature range 300-600 °C to the combustion of the TPA (Table 1). Highly crystalline samples show negligible loss below 300 °C, which reveals their hydrophobic nature. A similar weight loss was observed in the high temperature range corresponding to 4 TPA molecules per unit cell. The samples that were not fully crystalline (FS-100 and FS-50) showed higher water content and lower template content. Thus, there is a close correlation between the crystallinity of the samples and the results of thermal analysis.

The porosity and textural characteristics of the FS series of samples were determined by nitrogen (N_2) adsorption-desorption measurements at 77 K (Figure S12). The N_2 sorption isotherms of highly crystalline samples (FS-∞, FS-300, and FS-150) displayed the typical type I isotherm, characteristic of microporous materials.[22] These samples exhibit a second small uptake with hysteresis at about 0.1 P/P_0. Such additional hysteresis has already been reported for silicalite-1.[23] The most plausible explanation of this feature is the orthorhombic – monoclinic phase transition of the MFI-type framework.[22, 24] The micropore volume of these samples is 0.18 cm^3g^{-1}, which proves an excellent crystallinity. Lower micropore volume was recorded for FS-100 and FS-50, which is in line with the XRD analysis (Table 1).

The set of the physicochemical analyses shows that the properties of zeolites synthesized in an acidic fluorine-containing medium are similar to their counterparts obtained in a neutral medium using fluorine as a mineralizer.

The set of experimental data shows that it is possible to form a zeolite under acidic medium. The critical factor determining the ability of zeolite to crystallize under acidic conditions is the isoelectric point of silica, i.e., the surface charge of silica species. In the present case, the fumed silica with IEP around two readily transformed into MFI-type material in the pH range 2-5. Close to the IEP, the zeolite synthesis was still possible, but the crystallization rate slowed down, and only partial transformation of the initial system into zeolite was observed. Using a gel with pH below the IEP did not yield a zeolitic material since the surface charge of silica was reversed, which led to repulsive interactions with the structure-directing agent.

It should be noted the role of the F^- as mineralizer that dissolves silica source and transport the silica species to the structure directing agent. The solubility of silica is limited in most of mineral acids, which make them unappropriate for zeolite synthesis. Thus the HF acid and its derivatives are probably the sole option for zeolite synthesis in acidic medium.

The aluminum incorporation in zeolite framework is limited under acidic conditions, which is a consequence of the high IEP of alumina with respect to silica. Hence the introduction of heteroatoms in zeolite structure will strongly depend on their IEP, i.e., the surface charge of their species in acidic medium.

The present study opens the route to the acidic medium synthesis of zeolites. This pioneering work will have to be further deepened to reach a practical perspective, as the first issues are the incorporation of heteroatoms in the zeolite framework and the decrease of the crystal size. The recycling of fluoride effluent will be necessary to make the process environmentally benign.

UNDER EDIT

Acknowledgments

V.V., S.Q. and Q.F. acknowledge the support from the joint Sino-French international laboratory "Zeolites". V.V. acknowledges the talent start-up funding provided by QIBEBT. Q.F. thanks the National Natural Science Foundation of China (21571079, 21621001, 21390394, 21571076 and 21571078) for financial support.

Keywords: Acidic medium • Crystallization • MFI-type • Zeolite

[1] a) J. Y. Li, A. Corma, J. H. Yu, *Chem. Soc. Rev.* **2015**, *44*, 7112-7127; b) V. Valtchev, L. Tosheva, *Chem. Rev.* **2013**, *113*, 6734-6760; c) C. Martínez, A. Corma, *Coord. Chem. Rev.* **2011**, *255*, 1558-1580; d) S. Mintova, M. Jaber, V. Valtchev, *Chem. Soc. Rev.* **2015**, *44*, 7207-7233.

[2] A. Khamkeaw, M. Phisalaphong, B. Jongsomjit, K. A. Lin, A. C. K. Yip, *J. Hazard. Mater.* **2019**, 384, 121161.

[3] a) F. Dubray, S. Moldovan, C. Kouvatas, J. Grand, C. Aquino, N. Barrier, J.-P. Gilson, N. Nesterenko, D. Minoux, S. Mintova, *J. Am. Chem. Soc.* **2019**, *141*, 8689-8693; b) M. Smaihi, O. Barida, V. Valtchev, *Eur. J. Inorg. Chem.* **2003**, *2003*, 4370-4377; c) R. F. Lobo, S. I. Zones, M. E. Davis, *Journal of inclusion phenomena and molecular recognition in chemistry* **1995**, *21*, 47-78.

[4] P. Barrett, M. Camblor, A. Corma, R. H. Jones, L. Villaescusa, *J. Phys. Chem. B* **1998**, *102*, 4147-4155.

[5] Z. Qin, L. Lakiss, L. Tosheva, J.-P. Gilson, A. Vicente, C. Fernandez, V. Valtchev, *Adv. Funct. Mater.* **2014**, *24*, 257-264.

[6] R. M. Barrer, *Hydrothermal chemistry of zeolites*, Academic press, **1982**.

[7] R. M. Milton, Molecular sieve science and technology: a historical perspective. ACS Publications, Eds. M. L. Occeli & H. E. Robson, 1989, pp. 1-10.

[8] D. W. Breck, *Zeolite molecular sieves: structure, chemistry and use*, Wiley, New York, **1974**.

[9] E. M. Flanigen, R. L. Patton, United States Patent, No. 4073865, **1978**.

[10] a) J. Guth, H. Kessler, J. Higel, J. Lamblin, J. Patarin, A. Seive, J. Chezeau, R. Wey, ACS Publications, **1989,** pp. 176-195; b) J. Guth, H. Kessler, P. Caullet, J. Hazm, A. Merrouche, J. Patarin, in *Proceedings from the Ninth International Zeolite Conference*, Elsevier, **1993**, pp. 215-222; c) J. Guth, H. Kessler, R. Wey, in *Studies in Surface Science and Catalysis, Vol. 28*, Elsevier, **1986**, pp. 121-128.

[11] P. Caullet, J.-L. Paillaud, A. Simon-Masseron, M. Soulard, J. Patarin, *Comptes Rendus Chimie* **2005**, *8*, 245-266.

[12] B. Louis, L. Kiwi-Minsker, *Microporous Mesoporous Mater.* **2004**, *74*, 171-178.

[13] F. Ngoye, L. Lakiss, Z. Qin, S. Laforge, C. Canaff, M. Tarighi, V. Valtchev, K. Thomas, A. Vicente, J. P. Gilson, Y. Pouilloux, C. Fernandez, L. Pinard, *J Catal.* **2014**, *320*, 118-126.

[14] V. Eroshenko, R.-C. Regis, M. Soulard, J. Patarin, *J. Am. Chem. Soc.* **2001**, *123*, 8129-8130.

[15] a) F. L. Bleken, S. Chavan, U. Olsbye, M. Boltz, F. Ocampo, B. Louis, *Applied Catalysis A: General* **2012**, *447-448*, 178-185; b) O. Larlus, V. P. Valtchev, *Chem. Mater.* **2005**, *17*, 881-886.

[16] C. A. Fyfe, D. H. Brouwer, A. R. Lewis, J.-M. Chezeau, *J. Am. Chem. Soc.* **2001**, *123*, 6882-6891.

[17] a) O. B. Ayodele, H. F. Abbas, W. Daud, *Energy Conv. Manag.* **2014**, *88*, 1111-1119; b) C. I. Round, C. D. Williams, K. Latham, C. V. Duke, *Chem. Mater.* **2001**, *13*, 468-472.

[18] S. Mintova, V. Valtchev, *Microporous Mesoporous Mater.* **2002**, *55*, 171-179.

[19] J. Antonio Alves Júnior, J. Baptista Baldo, *New Journal of Glass and Ceramics* **2014**, *04*, 29-37.

[20] K. Gayer, L. Thompson, O. Zajicek, *Can. J. Chem.* **1958**, *36*, 1268-1271.

[21] H. Koller, A. Wölker, L. Villaescusa, M. Diaz-Cabanas, S. Valencia, M. Camblor, *J. Am. Chem. Soc.* **1999**, *121*, 3368-3376.

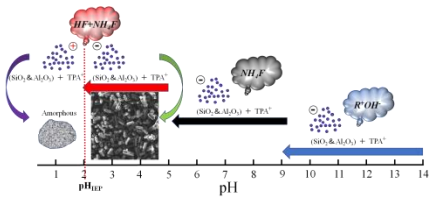
[22] K. A. Cychosz, R. Guillet-Nicolas, J. Garcia-Martinez, M. Thommes, *Chem. Soc. Rev.* **2017**, *46*, 389-414.

[23] a) U. Müller, K. Unger, in *Studies in Surface Science and Catalysis, Vol. 39*, Elsevier, **1988**, pp. 101-108; b) K. Nakai, J. Sonoda, M. Yoshida, M. Hakuman, H. Naono, *Adsorption* **2007**, *13*, 351-356.

[24] J. Parra, C. Ania, D. Dubbeldam, T. Vlugt, J. Castillo, P. Merkling, S. Calero, *J. Phys. Chem. C* **2008**, *112*, 9976-9979.

WILEY-VCH

Entry for the Table of Contents



This paper deals with the zeolite synthesis in acidic medium. The isoelectric point of silica source is found to be the critical factor controlling the zeolite formation under acidic conditions. The zeolite crystalizes solely at pH above the IEP when the silica particles are negatively charged.

WILEY-VCH