



Facile and fast determination of Si/Al ratio of zeolites using FTIR spectroscopy technique

Yik-Ken Ma, Severinne Rigolet, Laure Michelin, Jean-Louis Paillaud, Svetlana Mintova, Fitri Khoerunnisa, T. Jean Daou, Eng-Poh Ng

► To cite this version:

Yik-Ken Ma, Severinne Rigolet, Laure Michelin, Jean-Louis Paillaud, Svetlana Mintova, et al.. Facile and fast determination of Si/Al ratio of zeolites using FTIR spectroscopy technique. *Microporous and Mesoporous Materials*, 2021, 311, pp.110683. 10.1016/j.micromeso.2020.110683 . hal-02968402v1

HAL Id: hal-02968402

<https://hal.science/hal-02968402v1>

Submitted on 26 Nov 2020 (v1), last revised 28 Dec 2020 (v2)

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.

Facile and fast determination of Si/Al ratios of zeolites using FTIR spectroscopy technique

Yik-Ken Ma,^a Severinne Rigolet,^{b,c} Laure Michelin,^{b,c} Jean-Louis Paillaud,^{b,c} Svetlana

Mintova,^d Fitri Khoerunnisa,^e T. Jean Daou,^{b,c,*} Eng-Poh Ng^{a,*}

^a*School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia.*

^b*Université de Haute-Alsace, Axe Matériaux à Porosités Contrôlées, Institut de Science de Matériaux de Mulhouse UMR 7361, ENSCMu, 3b rue Alfred Werner, 68093 Mulhouse, France.*

^c*Université de Strasbourg, 67000 Strasbourg, France.*

^d*Laboratoire Catalyse & Spectrochimie, ENSICAEN, Université de Caen, 14000 Caen, France.*

^e*Chemistry Education Department, Universitas Pendidikan Indonesia, Jl. Setiabudhi 258, Bandung 40514, Indonesia.*

**Corresponding author. E-mail address: epng@usm.my (EPN); jean.daou@uha.fr (TJD)*

Abstract

A fast and simple quantitative determination of the Si/Al ratio (SAR) in zeolite frameworks using IR spectroscopy is reported. From the linear regression analysis, the Si/Al ratios correlate linearly to the corresponding wavenumbers (970-1090 cm⁻¹) for the medium-to-high Al content zeolites (1 < SAR < 5). The accuracy and validity of the IR model is also exemplified for 19 zeolites with different SAR and framework topologies. The quantitative determination of the SAR by the developed approach is shown to be an alternative technique to conventional ICP-OES and XRF spectroscopy techniques.

Keywords: Infrared spectroscopy; Zeolites; Si/Al ratio; Vibration bands; Quantitative analysis

1. Introduction

Zeolites are very important and useful industrial materials used in adsorption, separation and catalysis due to their various micropore sizes and unique framework properties [1-3]. Besides the structural properties, the Al content in the framework or so-called Si/Al ratio (SAR) is also important since it governs the surface properties of zeolites and affecting their application performances, particularly in the catalytic reactions and adsorption phenomena [4,5].

In general, the most common diagnostic physical techniques for the identification of Al content in zeolites are X-ray fluorescence spectroscopy (XRF), atomic absorption spectroscopy (AAS), inductively coupled plasma atomic emission spectroscopy (ICP-OES), X-ray diffraction (XRD) and solid state ^{29}Si nuclear magnetic resonance (^{29}Si NMR). However, these analytical tools face some limitations particularly in measurement time length, sample recovery after measurement, amount of sample used, sample preparation workout and post-analytical interpretation treatment (Table 1). Therefore, the development of fast, simple and reliable method for quantitatively determining the Al content in the zeolite framework is always welcome.

Fourier-transform infrared spectroscopy (IR) is often used to study the functional groups, zeolite structure, secondary building units (SBUs) and pore openings of molecular sieves. Typically, the mid IR region of 200 to 1300 cm^{-1} is a sensitive area revealing the fundamental vibrations of structural framework of zeolites. In past few decades, several efforts have been initiated to study zeolites by using IR spectroscopy [6-9]. In 1970s, Wright et al. [6] and Flanigen et al. [7] reported a detailed and systematic spectroscopy studies on various aluminosilicate zeolites. They found out the positions of certain IR bands at 970-1020 cm^{-1} , 670-725 cm^{-1} , 565-580 cm^{-1} and 360-385 cm^{-1} responded linearly with the Al content in faujasite zeolites. Since then, Lohse et al. reported the use of the IR band at 748-837 cm^{-1} to

calculate the SAR of cubic and hexagonal faujasite zeolites [8]. However, the validity of IR spectroscopy method for identifying the SAR is only limited to faujasites. Hence, the development of theoretical calculations using IR spectroscopy to determine the SAR in various zeolite frameworks is still not yet developed and remain unclear.

In this communication, we report and develop a very simple and fast IR spectroscopy protocol for determining the SAR in various types of zeolites.

2. Experimental

2.1. Analytical procedures

19 types of zeolites with various framework topologies and Si/Al ratios were selected and synthesized as reported in ref. [11-25] (See Supplementary Information). The FTIR spectra of the zeolites were recorded with a Perkin Elmer's System 2000 IR spectrometer (1400 to 400 cm^{-1} , resolution of 2 cm^{-1} , 100 scans) using the KBr pellet technique.

The chemical composition of samples was determined using a Varian Vista MPX ICP-OES and XGT-5200 XRF spectrometers. For ICP-OES spectroscopy analysis, the zeolite powder (0.0005 g) was first dissolved and stirred in HF solution (2 mL, 39%, Merck) for at least 12 h under stirring before dilution and filtration using 0.45- μm microfilter. Boric acid was added to minimize fluoride interferences during measurement. For ^{29}Si MAS NMR spectroscopy measurement, the analysis was performed with a Bruker Avance II 300 MHz spectrometer according to the procedure reported in ref [26] and the Si/Al ratio was calculated using Equation (1) [27]:

$$\text{Si / Al} = \frac{\sum_{n=0}^4 I_{\text{Si}(n\text{Al})}}{\sum_{n=0}^4 (n / 4) I_{\text{Si}(n\text{Al})}} \quad (1)$$

Where n is the number of adjacent Al nuclei, I is the relative intensity of each ^{29}Si NMR spectrum signals (Q^0 – Q^4).

3. Results and discussion

The IR spectra of selected zeolites (Na-ZSM-5, Na-Beta, Na-mordenite, Na-EMC-2, K-L and Na-X) containing a broad range of SAR are shown in Fig. 1. As seen, each zeolite has a specific fingerprint spectrum from 400-820 cm^{-1} which is due to their distinct framework structures [28]. However, those bands are unable to be used for determining the SAR due to their different secondary building units and framework structures. Nevertheless, the band at around 970-1090 cm^{-1} , which is due to asymmetric stretching mode of Si-O-T ($T = \text{Si}$ or Al) [29], is present in all zeolite samples. This band is very sensitive and shifted when the zeolites have different framework Al contents. In order to prove it, the SAR of these samples are quantitatively measured with ICP-OES spectroscopy and the correlation between the SAR and the position of this IR band absorbed at the minimum transmittance is plotted (Fig. 1b). It can be seen that the SAR values correlate linearly to the corresponding wavenumbers with overall regression coefficient $R^2 = 0.9993$. Nevertheless, the correlation dramatically fluctuates when the Si/Al ratio exceeds 5 because the shape of this IR band tends to deform when more Al atoms are substituted with Si atoms. As a result, this IR band will overlap with another IR band of T-O stretching mode at around 1100 cm^{-1} [30]. Thus, the linear equation of $y = 0.0458x - 43.584$, where y is the SAR and x is the asymmetric stretching frequency of Si-O-T in cm^{-1} , can be used to determine the SAR value in medium-to-high Al content zeolites ($1 < \text{SAR} < 5$).

The occurrence of IR band shifting is related to the vibration, length and angle of Si-O-T bond in zeolites where different distribution of Si and Al atoms in the framework structures also affects the chemical environment of Si. Hence, ^{29}Si MAS NMR spectroscopy, which is an

established method in determining the Si/Al ratio in zeolites, is used for validation of the above correlation. For those six samples, the different distributions of Q_n units are shown in the ^{29}Si MAS NMR spectra and the SAR values are calculated after deconvolution (Fig. 2a). Interestingly, the SAR values determined by IR and ^{29}Si MAS NMR spectroscopy methods are relatively close for the zeolites that have SAR less than 5, thus showing [good correlation with](#) ICP-OES, IR and NMR spectroscopy methods (Fig. 2b).

[In should be mentioned here that the IR and \$^{29}\text{Si}\$ NMR spectroscopies measure the SAR of zeolite frameworks. Hence, it is also important to use other techniques, such as XRF and ICP-OES spectroscopies, that measure the total SAR of zeolites that includes the non-framework species \(if present\).](#) Thus, the accuracy of IR spectroscopy method is exemplified in other types of zeolites having SAR values containing medium-to-high Al content ($1 < \text{SAR} < 5$) and validated using conventional XRF and ICP-OES spectroscopy techniques. As seen in Table 2, the values estimated using IR method are nearly close to those measured with XRF and ICP-OES spectroscopy methods except the SAR value for zeolite A. The results in Table 2 are further applied and interpreted in the linear regression analysis excluding zeolite A sample (Figure 3). Interestingly, the correlation coefficient for IR spectroscopy against ICP-OES spectroscopy methods (the most sensitive analytical tool) is found to be highly satisfactory (R^2 values = 0.967) with considerably low scattering of data points for SAR in the range tested. On the other hand, the linear regression model between IR and XRF spectroscopy methods works reasonably acceptable with R^2 values = 0.975. Hence, this study presents a fast and simple technique complementary to the conventional ICP-OES, XRF and ^{29}Si MAS NMR spectroscopy for determination of the Si/Al ratio in zeolites.

Acknowledgement

The financial support from RUI (1001/PKIMIA/8011128) and Institut Universitaire de France (IUF) is gratefully acknowledged.

References

- [1] I. Deroche, T. J. Daou, C. Picard & B. Coasne, *Nat. Commun.* 10 (2019) 1-10.
- [2] G. Majano, E.-P. Ng, L. Lakiss, S. Mintova, *Green Chem.* 13 (2011) 2435-2440.
- [3] S.-F. Wong, K. Deekomwong, J. Wittayakun, T.C. Ling, O. Muraza, F. Adam, E.-P. Ng, *Mater. Chem. Phys.* 196 (2017) 295-301.
- [4] Y. Jiang, L. Zhang, Y. Xie, S. Han, Q. Zhu, X. Meng, F.-S. Xiao, *Catal. Today*, In press
- [5] C. Keawkumay, W. Rongchapo, N. Sosaa, S. Suthirakun, I.Z. Koleva, H.A. Aleksandrov, G.N. Vayssilov, J. Wittayakun, *Mater. Chem. Phys.* 238 (2019) 121824.
- [6] A.C. Wright, J.P. Rupert, W.T. Granquist, *Am. Mineralogist* 53 (1968) 1293-1303.
- [7] E.M. Flanigen, H. Khatami, H.A. Szymanski, In *Molecular Sieve Zeolites-I*; E.M. Flanigen, L.B. Sand, Eds.; *Advances in Chemistry*; American Chemical Society: Washington, 1974; Vol. 101; Chapter 16, pp 201-229.
- [8] U. Lohse, I. Pitsch, E. Schreier, B. Parltitz, K.-H. Schnabel, *Appl. Catal. A: Gen.* 129 (1995) 189-202.
- [10] W. Mozgawa, M. Krol, K. Barczyk, *Chemik* 65 (2011) 667-674.
- [11] T.M.A. Ghrear, S. Rigolet, T.J. Daou, S. Mintova, T.C. Ling, S.H. Tan, E.-P. Ng, *Micropor. Mesopor. Mater.* 277 (2019) 78-83.

- [12] N.H. Ahmad, T.J. Daou, P. Maireles-Torres, M. Zaarour, S. Mintova, T.-C. Ling, E.-P. Ng, *Mater. Chem. Phys.* 244 (2020) 122688.
- [13] S.-F. Wong, H. Awala, A. Vincente, R. Retoux, T.C. Ling, S. Mintova, R.R. Mukti, E.-P. Ng, *Micropor. Mesopor. Mater.* 249 (2017) 105-110.
- [14] IZA-SC Database of zeolite synthesis. <http://www.iza-online.org/synthesis/Recipes/EMC-2.html>
- [15] Y.-W. Cheong, K.-L. Wong, T.C. Ling, E.-P. Ng, *Mater. Exp.* 8 (2018) 463-468.
- [16] E.-P. Ng, G.K. Lim, G.-L. Khoo, K.-H. Tan, B.S. Ooi, F. Adam, T.C. Ling, K.L. Wong *Mater. Chem. Phys.* 155 (2015) 30-35.
- [17] G. J. Kim, W. S. Ahn, *Zeolites* 11 (1991) 745-750.
- [18] E.-P. Ng, L. Delmotte, S. Mintova, *ChemSusChem* 2 (2009) 255-260.
- [19] M.-Y. Choo, J.C. Juan, L.E. Oi, T.C. Ling, E.-P. Ng, A.R. Noorsaadah, G. Centi, K.T. Lee, *Catal. Sci. Technol.* 9 (2019) 772-782.
- [20] E.-P. Ng, D. Chateigner, T. Bein, V. Valtchev, S. Mintova, *Science* 335 (2012) 70-73.
- [21] G. H. K hl, *Zeolites* 7 (1987) 451-457.
- [22] A. Cichocki, P. Koscielniak, *Micropor. Mesopor. Mater.* 29 (1999) 369-382.
- [23] L.V.C. Rees, S. Chandrasekhar, *Zeolites* 13 (1993) 535-541.
- [24] A. Astafan, M.A. Benghalem, Y. Pouilloux, J. Patarin, N. Bats, C. Bouchy, T.J. Daou, L. Pinard, *J. Catal.* 336 (2016) 1-10.

- [25] T. Crémoux, I. Batonneau-Gener, A. Moissette, J.-L. Paillaud, M. Hureau, E. Ligner, C. Morais, S. Laforge, C. Marichal, H. Nouali, *Phys.Chem.Chem.Phys.* 21 (2019) 14892.
- [26] E.-P. Ng, H. Awala, J.-P. Ghoy, A. Vicente, T.C. Ling, Y.H. Ng, S. Mintova, F. Adam, *Mater. Chem. Phys.* 159 (2015) 38-45.
- [27] G. Engelhardt, U. Lohse, V. Patzelová M.Mägi, E. Lippmaa, *Zeolites* 3 (1983) 233-238.
- [28] C.A.R. Reyesa, C. Williams, O.M.C. Alarcón, *Mater. Res.* 16 (2013) 424-438.
- [29] B. Herreros, J. Klinowski, *J. Chem. Soc. Faraday Trans.* 91 (1995) 1147-1154.
- [30] K. Byrappa, B.V.S. Kumar, *Asian J. Chem.* 19 (2007) 4933-4935.

Credit authorship contribution statement

Yik-Ken Ma: Writing - original draft, Synthesis, Analysis, Data interpretation. **Severinne Rigolet:** Analysis, Data interpretation. **Laure Michelin:** Analysis. **Jean-Louis Paillaud:** Synthesis. **Svetlana Mintova:** Analysis, Writing - review & editing. **Fitri Khoerunnisa:** Synthesis. **T. Jean Daou:** Synthesis, Analysis, Data interpretation, Writing - review & editing. **Eng-Poh Ng:** Supervision, Data interpretation, Writing - review & editing, Project administration.

Figure captions

Fig. 1. (A) The IR spectra and Si/Al ratio (in bracket) of (a) Na-ZSM-5 (14.8), (b) Na-Beta (13.5), (c) Na-mordenite (4.93), (d) Na-EMC-2 (3.80), (e) K-L (3.21) and (f) Na-X (1.16) zeolites, and (B) linear regression analysis of Si/Al ratio versus wavenumber.

Fig. 2. (A) ^{29}Si MAS NMR spectra of (a) Na-ZSM-5, (b) Na-Beta, (c) Na-mordenite, (d) Na-EMC-2, (e) K-L and (f) Na-X zeolites, and (B) linear regression correlation of the Si/Al ratios estimated by IR spectroscopy and validation by ^{29}Si MAS NMR spectroscopy.

Fig. 3. IR regression linearity assessment of SAR validated using (a) ICP-OES and (b) XRF spectroscopy techniques for 16 different zeolite topologies.

Figures

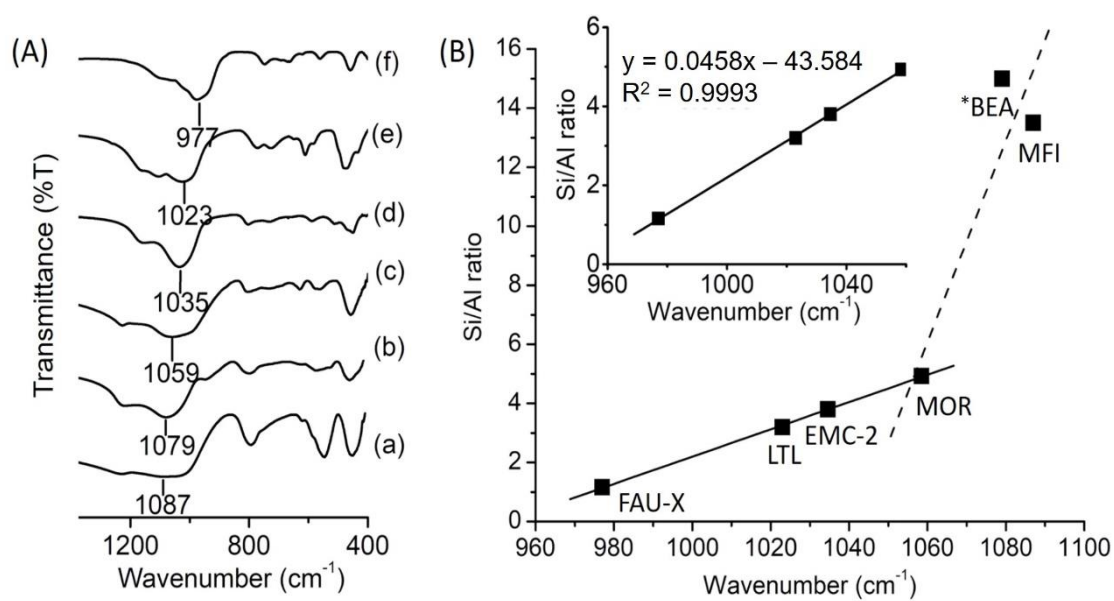


Fig. 1.

Table captions

Table 1. Advantages (✓) and disadvantages (×) of various spectroscopy techniques used for determination of the SAR of zeolites.

Table 2. The position corresponding asymmetric stretching Si-O-T (T = Si or Al) bands at 950-1090 cm^{-1} (x) used for estimation of the SAR of zeolites (y) using linear regression equation: $y = 0.0458x - 43.584$, and the SAR values determined by ICP-OES and XRF spectroscopy.

Tables

Table 1.

	ICP-OES	AAS	XRF	XRD	IR	²⁹Si NMR
Sample recovery	×	×	√	√	√	√
Fast analysis	×	×	×	×	√	×
Small sample quantity required	√	√	×	×	√	×
Simple sample preparation	×	×	√	√	√	√
Post-treatment requirement	×	×	×	√	×	√

Table 2.

No.	Zeolites	Framework code	Wavenumber (cm ⁻¹)	Si/Al ratio		
				IR ^a	ICP-OES	XRF
1.	K-F	EDI	973	0.98	1.26	1.02
2.	Cs-ABW	ABW	985	1.53	1.03	1.13
3.	Na-EMT	EMT	980	1.30	1.16	1.18
4.	K-W	MER	992	1.85	2.30	2.19
5.	K-L	LTL	1023	3.27	3.20	2.93
6.	K-J	LTJ	987	1.62	1.86	1.77
7.	Na-Mordenite	MOR	1059	4.92	4.93	4.88
8.	Na-X	FAU	977	1.16	1.16	1.18
9.	Na-Y	FAU	996	2.03	1.98	2.13
10.	Na-EMC-2	EMT	1035	3.82	3.76	3.71
11.	Hydroxysodalite	SOD	983	1.44	1.10	1.14
12.	Na-A	LTA	952	0.02	1.04	0.98
13.	Heulandite	HEU	1026	3.41	3.50	3.48
14.	Brewsterite	BRE	1012	2.77	3.00	2.91
15.	Na-LSX	FAU	973	0.98	0.98	1.03
16.	Offretite	OFF	1037	3.91	3.89	3.76
17.	Na-P	GIS	983	1.44	1.35	1.44
18.	Na-BEA	*BEA	1083	6.02	15.1	15.0
19.	Na-ZSM-5	MFI	1088	6.25	13.5	12.2

Supporting Information

1. Experimental

1.1. Chemicals

The silica sources used in the zeolite syntheses were colloidal HS-40 (LUDOX, 40% SiO₂, Sigma-Aldrich), sodium metasilicate pentahydrate (Na₂SiO₃·5H₂O, 95%, Sigma-Aldrich), silica sol (30% SiO₂, VP 4039, Bayer AG), silica powder (Zeosil from Kofran Co., 91.8% SiO₂, 8.2% H₂O), sodium silicate (27% SiO₂, 8% Na₂O, Merck), silica sol (29.5% SiO₂, 0.2% Na₂O, Rudniki Chemical Works) and fume silica (99.8% SiO₂, Sigma-Aldrich). On the other hand, the alumina sources used were sodium aluminate (53% Al₂O₃, 42.5% Na₂O, Sigma-Aldrich), sodium aluminate (56.2% Al₂O₃, 39.5% Na₂O, Strem Chemicals), aluminum hydroxide (100% Al₂O₃, Acros Organics), aluminum shavings and aluminum sulfate hexadecahydrate (97% purity, BDH Chemicals). Sodium fluoride, sodium chloride, sulfuric acid (~96%) and kaolinite (Al₂O₃:2.2SiO₂:2H₂O) were purchased from Sigma-Aldrich. The inorganic templates used were potassium hydroxide (85% purity, QRĕC), sodium hydroxide (99% purity, QRĕC) or cesium hydroxide monohydrate (99.5% purity, Sigma-Aldrich) while 18-crown-6 ether (99% purity, Sigma-Aldrich), tetrapropylammonium bromide (TPABr, 98%, Fluka) were used as the organic templates.

1.2. Synthesis of zeolites

19 types of zeolites with different topologies, namely K-F, Cs-ABW, Na-EMT, K-W, K-L, K-J, Na-mordenite, Na-X, Na-Y, Na-EMC-2, hydroxysodalite, Na-A, Na-LSX, offretite, Na-P, Na-BEA, Na-ZSM-5, heulandite and brewsterite were synthesized by using the chemical compositions and the heating conditions as shown in Table S1 where the detailed synthesis procedures were described in Section 1.2.1–1.2.17.

Table S1. The chemical compositions and conditions for synthesis of zeolites.

Zeolite	Topology	Hydrogel precursor composition				Heating condition		Ref.
		SiO ₂	Al ₂ O ₃	Template	H ₂ O	T (°C)	t (h)	
Cs-ABW	ABW	4	1	16 Cs ₂ O	164	180	3	[10]
KL	LTL	20	1	10 K ₂ O	800	30	18 ^a	[11]
						180	72	
K-F	EDI	4	1	16 K ₂ O	160	100	4	[12]
EMC-2	EMT	10	1	2.2 Na ₂ O & 0.87 18-crown-6	140	25	24 ^a	[13]
						120	288	
K-W	MER	7	1	3.5 K ₂ O	196	180	14	[14]
K-J	LTI	3.75	1	15 K ₂ O	132	120	30	[15]
Na-mordenite	MOR	30	1	6Na ₂ O	780	170	24	[16]
Na-X	FAU	5	1	20 Na ₂ O	700	30	24 ^a	[17]
						50	58	
Na-Y	FAU	18	1	10 Na ₂ O	300	40	6 ^a	[18]
						90	20	
Na-EMT	EMT	5	1	17.48 Na ₂ O	340	30	36	[19]
Hydroxy-sodalite	SOD	5	1	17.48 Na ₂ O	340	30	0.25 ^b	[19]
Na-A	LTA	1.5	1	6 Na ₂ O	300	90	9	[20]
LSX	LSX	2.2	1	5.5 Na ₂ O & 1.65 K ₂ O	122	100	2	[21]
Offretite	OFF	16.5	1	4.18 Na ₂ O & 1.25 K ₂ O	175	140	168	[22]
Na-P	GIS	2.2	1	5.28 NaF	106	85	1440	[23]
Na-Beta	*BEA	50	1	0.7 Na ₂ O & 9 (TEA) ₂ O	554	95	216	[24]
Na-ZSM-5	MFI	30.30	1	61.05 Na ₂ O & 9.84 (TPA) ₂ O	1273	210	12	[25]
Heulandite	HEU	-----Natural zeolite-----						
Brewsterite	BRE	-----Natural zeolite-----						

^aaging; ^bMicrowave heating at 200 W

1.2.1. K-F zeolite (EDI)

The aluminate solution was prepared by adding 6.400 g of potassium hydroxide into 16.500 g of distilled water followed by 1.950 g of aluminum hydroxide. A clear aluminate solution was obtained after heating (100 °C, 12 h) and continuous stirring (400 rpm). The silicate solution was prepared by mixing 20.000 g of potassium hydroxide with 15.000 g of distilled water followed by 7.500 g of colloidal HS-40. The aluminate solution was then slowly added into the silicate solution under continuous vigorous stirring (400 rpm). Homogeneity was then achieved through hand-stirring using a spatula. The gel-like precursor obtained was immediately transferred to a polypropylene bottle and heated at 100 °C for 4 h.

1.2.2. Cs-ABW zeolite (ABW)

The aluminate solution was prepared by first mixing 3.500 g of cesium hydroxide monohydrate and 0.414 g of aluminum hydroxide in 2.688 g of distilled water. The mixture was then heated at 105 °C for 16 h under continuous stirring (400 rpm) to obtain a clear solution. The silicate solution was prepared by dissolving 1.594 g of HS-40 and 10.763 g of cesium hydroxide monohydrate in 2.663 g of distilled water.

1.2.3.. Na-EMT zeolite (EMT)

Initially, the aluminate solution was first prepared by dissolving 9.074 g of sodium aluminate (Strem Chemicals) and 1.61 g of sodium hydroxide in 100.00 g of distilled water.

The clear solution was then added with 44.00 g of sodium hydroxide under stirring in an ice bath. A clear aluminate solution was obtained. Next, the clear silicate solution was prepared by mixing and stirring 57.69 g of sodium silicate and 20.00 g of sodium hydroxide in 80.00 g of distilled water. The aluminate solution was then slowly added into the silicate solution under continuous stirring for 5 min before the resulting precursor was crystallized at 30 °C for 36 h.

1.2.4. K-W zeolite (MER)

First, the aluminate solution was prepared by mixing 3.406 g of potassium hydroxide, 1.162 g of aluminum hydroxide with 9.377 g of distilled water. The mixture was then heated for 105 °C for 12 h under stirring (400 rpm) in order to dissolve insoluble aluminum hydroxide. The silicate solution was prepared by mixing 7.750 g of colloidal HS-40 with 12.000 g of distilled water. The aluminate solution was then added into the silicate source. Next, the mixture was mechanically stirred for 15 min using a spatula. The mixture was transferred to a 50-mL stainless-steel autoclave and subjected to hydrothermal heating at 180 °C for 14 h.

1.2.5. K-L zeolite (LTL)

The aluminate solution was prepared by first dissolving 1.442 g of aluminum sulfate hexahydrate in 18.208 g of distilled water before 3.018 g of potassium hydroxide was added. Then, 6.875 g of colloidal HS-40 and 9.958 g of distilled water were mixed to produce the silicate solution. The silicate solution was then added slowly into the aluminate source solution under continuous stirring (400 rpm). The mixture was aged at room temperature for 18 h before being heated at 180 °C for 72 h.

1.2.6. *K-J zeolite (LTJ)*

The aluminate solution was prepared by mixing 6.460 g of potassium hydroxide and 1.950 g of aluminum hydroxide in 16.280 g of distilled water. It was then immediately heated at 105 °C for 12 h under continuous stirring (400 rpm) to obtain a clear aluminate solution. The silicate solution was prepared by mixing 19.38 g of potassium hydroxide and 7.320 g of colloidal HS-40 with 6.458 g of distilled water. The silicate solution was slowly added into the aluminate solution. Homogeneity of the mixture was achieved through vigorous hand-stirring using spatula (15 min). The crystallization was then initiated at 120 °C for 30 h using a 50-mL stainless-steel autoclave.

1.2.7. *Na-mordenite zeolite (MOR)*

Initially, 1.88 g of sodium hydroxide was dissolved in 4.00 g of distilled water before 0.96 g of sodium aluminate (Sigma-Aldrich) was added. The clear solution was then added with 64.5 g of distilled water before 9.82 g of silica was introduced. The final hydrogel was stirred for another 30 min before it was autoclaved and crystallized at 170 °C for 24 h.

1.2.8. *Na-X zeolite (FAU)*

The aluminate solution was prepared by mixing 15.000 g of sodium hydroxide and 3.200 g of sodium aluminate (Sigma-Aldrich) in 33.300 g of distilled water. For the preparation of silicate solution, 8.170 g of sodium hydroxide was first added into 164.300 g distilled water

followed by the addition of 18.514 g of sodium silicate. The aluminate solution was slowly added into the silicate solution under continuous stirring (400 rpm, 15 min). The hydrogel was then aged at 30 °C for 24 h before subjecting to crystallization at 50 °C for 58 h.

1.2.9. Na-Y zeolite (FAU)

The aluminate solution was prepared by adding 0.889 g of sodium aluminate (Sigma-Aldrich) into 4.000 g of distilled water. The silicate solution was obtained by mixing 1.311 g of sodium hydroxide, 8.927 g of distilled water with 18.514 g of sodium silicate. Then, the aluminate solution was slowly added into the silicate solution under stirring (400 rpm). The resulting hydrogel mixture was aged at 40 °C for 6 h before crystallizing at 90 °C for 20 h.

1.2.10. Na-EMC-2 zeolite (EMT)

The hydrogel was first prepared by mixing 6.05 g of NaOH solution (50%), 7.26 g of sodium aluminate (Strem Chemicals), 8.81 g of 18-Crown-6 ether in 39.00 g of water. The mixture was magnetically stirred until dissolved before 77.00 g of silica sol was added. The resulting hydrogel was aged at room temperature for a day before it was transferred to a stainless-steel autoclave for crystallization at 110 °C for 12 days.

1.2.11. Hydroxysodalite zeolite (SOD)

The synthesis was similar to the synthesis of Na-EMT zeolite reported in section 1.2c except during crystallization process where Anton Paar Synthos 3000 microwave synthesizer was used to heat the precursor at 30 °C for 15 min using 200 W microwave power.

1.2.12. Na-A zeolite (LTA)

Initially, 7.126 g of sodium aluminate (Sigma-Aldrich) was mixed with 50.000 g of distilled water in order to prepare a clear aluminate solution. The silicate solution was then prepared by mixing 12.716 g of sodium hydroxide, 12.3631 g of sodium silicate with 141.964 g of distilled water. The aluminate solution was then slowly added into the silicate solution under stirring (400 rpm, 15 min) before the resulting precursor was heated at 90 °C for 9 h for crystallization.

1.2.13. Na-LSX zeolite (FAU)

Typically, 7.2783 g of sodium aluminate (Sigma-Aldrich) was dissolved in 30.000 g of distilled water to obtain a clear aluminate solution. Another solution was also prepared by dissolving 10.847 g of sodium hydroxide and 8.240 g of potassium hydroxide in 41.636 g of distilled water. These two solutions were then mixed together under stirring (400 rpm). The resulting clear solution was then slowly added into 18.519 g of sodium silicate under continuous stirring (400 rpm). The mixture was then heated at 100 °C for 2 h for crystallization.

1.2.14. Offretite zeolite (OFF)

Typically, 4.67 g of sodium hydroxide and 3.24 g of potassium hydroxide were dissolved in 9.57 g of distilled water and the resulting solution was cooled down to room temperature. Then 67.00 g of silica sol was added to these solution and stirred vigorously for 5 min. Finally, sodium aluminate solution (26.6 wt% Al_2O_3 , 19.6 wt% Na_2O prepared by the reaction of aluminum shavings with concentrated sodium hydroxide solution (~30 wt% NaOH) was added drop by drop to the stirred silicate over 10 min interval and the stirring was maintained for 20 min. The mixture was then aged for 24 h without stirring. The mixture was then transferred into stainless steel autoclave and heated at 140 °C for 7 days for crystallization.

1.2.15. Na-P zeolite (GIS)

In a bottle of polypropylene, 10.4 g of sodium fluoride were dissolved in 87.7 g of distilled water under stirring. Then 12.7 g of kaolinite were added to the obtained solution under stirring. The obtained mixture was then heated at 85 °C for 60 days.

*1.2.16. Na-Beta zeolite (*BEA)*

Initially, a transparent silicate solution was prepared by adding 25.00 g of colloidal AS-40 and 25.33 g of TEAOH into 1.88 g of distilled water. A clear aluminate solution was prepared by mixing 0.35 g of aluminum isopropoxide and 0.19 g of sodium hydroxide into 2.00 g of distilled water. The aluminate solution was then slowly added into the silicate solution under stirring (420 rpm) before being crystallized at 95 °C for 9 days in a polypropylene bottle. The resulting milky solution of BEA zeolite was purified by several centrifugation-dispersion cycles in distilled water (20000 rpm for 30 min). The final sample was calcined under air at 550 °C for 5 h with a temperature ramp of 1 °C min⁻¹.

1.2.17. Na-ZSM-5 zeolite (MFI)

Initially, 7.45 g of TPABr and 6.00 g of sodium chloride were dissolved in 30.00 g of distilled water and mixed with 0.94 g of aluminum sulfate hexadecahydrate. Then, a solution of 10.52 g of sodium metasilicate pentahydrate was added. After dissolution of the precipitate, a solution containing 7.00 g of TPABr, 0.43 g of sodium hydroxide and 3.00 g of sodium chloride was finally added. The pH was adjusted to 10 by dropwise addition of sulfuric acid and the mixture was stirred vigorously for 12 h before it was hydrothermally treated at 210 °C for 12 h in a 700 mL MaxiTech steel autoclave equipped with a PID temperature controller.

1.3. Purification of zeolite solid products

After hydrothermal crystallization process, the zeolite solids obtained from Section 1.2.1–17 were washed using distilled water by centrifugation (10000 rpm, 10 min) until pH 7 was reached. The zeolite suspensions were then freeze-dried in order to obtain fine powdered samples.

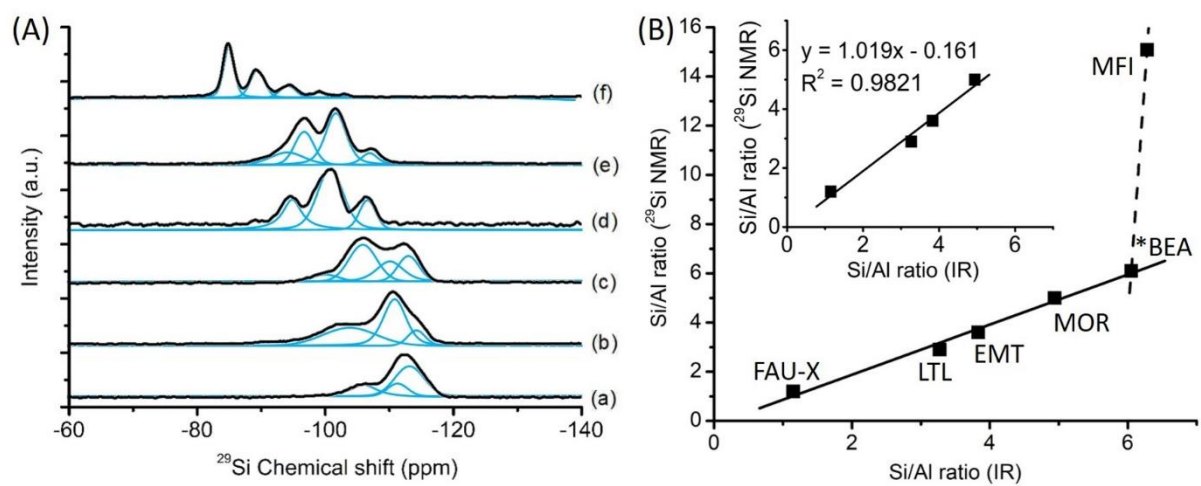


Fig. 2.

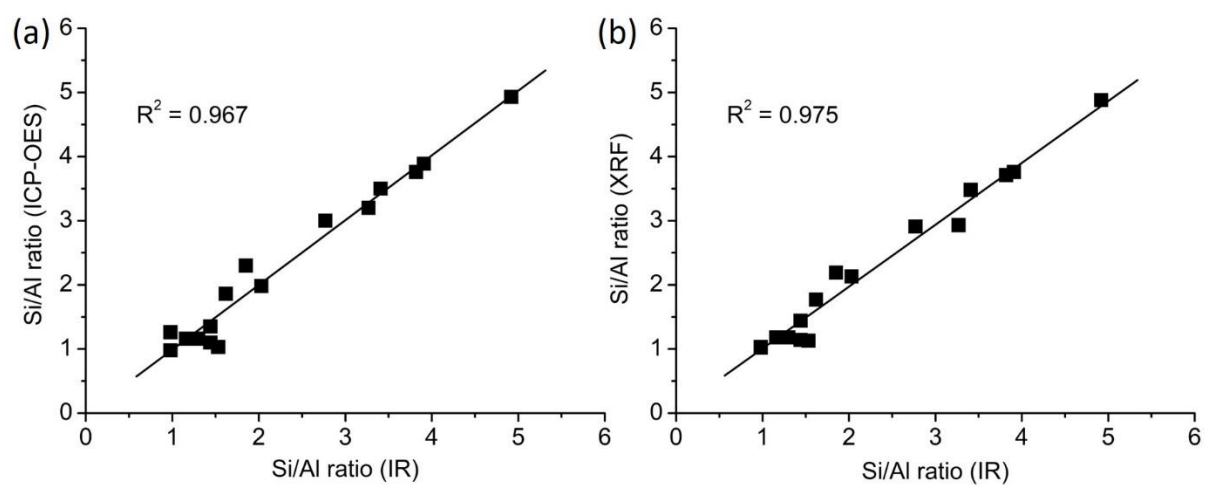


Fig. 3.