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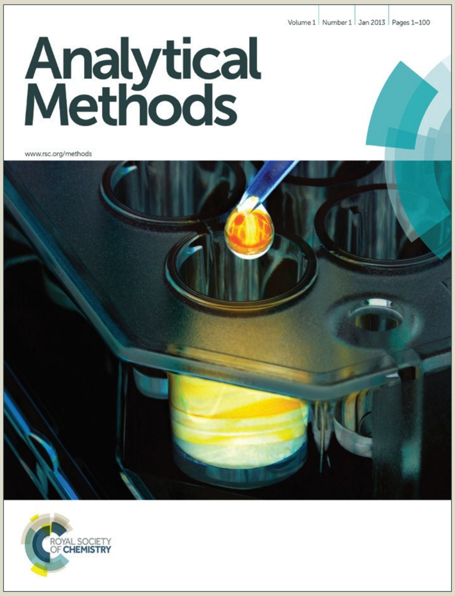

Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Analytical Methods

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Analytical Methods

ARTICLE

Received 00th January 20xx,
Accepted 00th January 20xx
DOI: 10.1039/x0xx00000x
www.rsc.org/

Facile evaluation of the crystallization of nano ZSM-5 using Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy and multivariate curve resolution- alternating least squares

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Nano-crystal ZSM-5 was fabricated through reflux crystallization method under atmospheric pressure and crystallization evolutionary process was investigated utilizing Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy. Control of crystallization process and understanding of the growth mechanism of nano crystals is considerable in developing technological applications. It was aimed to compare the outcome of proposed approach as an alternative with this of XRD. Multivariate curve resolution-alternating least squares (MCR-ALS) was employed to resolved the DRIFT spectral data set providing the evolution trend of crystallization process using Evolving Factor Analysis (EFA) as initial estimate approach of concentration profiles. The non- parametric Wilcoxon signed rank test (t-test) was applied to evaluate the obtained results which it confirmed reasonable agreement between two methods.

Introduction

Aluminosilicate H-ZSM-5 zeolite has been used in wide range of chemical processes, such as xylene isomerization [1], fluid catalytic cracking [2] and methanol to gasoline conversion [3]. It is known as useful candidate catalyst for methanol to propylene (MTP) process [4-5]. It has a medium size pore system with two channels, both including 10-ring. Straight channels (5.1- 5.5A˚) are intersected by zigzag channels (5.3-5.6A˚), thus creating a three-dimensional network [6]. Many applications of ZSM-5 could be improved by controlling its particle size. As an example, nano size ZSM-5 has shown better performance compared to the micro ZSM-5 during the MTP reaction [7-8].

As the characteristics of nanocrystalline ZSM-5 is highly dependent on its synthesis condition, it should be optimized. In order to achieve this purpose, studying the mechanism of crystallization evolution is crucial for controlled synthesis. The sophisticated standard X-ray powder diffraction (XRD) technique is used for quantitative and qualitative assessment of zeolite crystallization which is time consuming with high cost. However spectrophotometric analyses are usually fast, cost effective and easy to perform but there is the problem of spectral overlapping in these investigations. The problem of spectral overlapping and data interferences can be overcome utilizing different chemometrics techniques. Recently application of chemometric approaches in nano material synthesis by spectroscopy has been increased and several papers have been published. Investigation of shape evolution mechanism of CdSe quantum dots [9], detection of intermediate particles in the growth of zinc oxide nanoparticles [10] and determination of nanoparticles concentration [11] are some of the recent reports in this field.

Multivariate curve resolution- alternating least squares (MCR-ALS) is known as a soft modelling chemometric approach to obtain pure concentration and pure spectral profiles of all components in a chemical process [12].

Although spectroscopic evaluations in combination with chemometrics has been previously established to study the structure of nanoparticles but it has been mostly based on UV/Vis spectroscopy and there is no report on application of FTIR spectroscopy for this aim till now.

Considering infrared spectrometric analysis of ZSM-5 by the conventional transmission method, it is difficult to prepare a very thin self-supported wafer. Therefore, the special sample holder and cell is required which should be designed. Thus diffuse reflectance spectroscopy is commonly utilized for the analysis of zeolite powder samples.

Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy is much more sensitive in comparison with the standard transmittance spectroscopy [13] and utilizing chemometrics approaches has been here proposed to provide an easy route for fast monitoring of ZSM-5 nano particles evolution because of the simplicity, speed, and low cost of spectrophotometric measurements.

Therefore in this work DRIFT spectra of powdered samples were recorded to be processed for monitoring the evolution process of the ZSM-5 nanocrystals formation by spectra analysis of solid products obtained at different times during reflux synthesis.

The DRIFT analysis of the samples needs to be performed after preheating in a vacuum for dehydration or in situ high-temperature diffuse reflectance cell is necessary to ensure that samples are dehydrated. Considering the moisture adsorption

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x by sample, the spectral region below 1000 cm^{-1} was selected to eliminate the water related vibrations [14]. Furthermore in order to avoid the role of other precursor's spectral signals such as organic template which may impose complexity in the IR pattern and ensure exclusive spectral feature of the reaction components, it was necessary to limit at the spectral region.

In this work, DRIFT spectroscopy was proposed to be employed as monitoring approach for investigation of progress in fabrication of ZSM-5 nanocrystals, prepared through reflux crystallization method using tetrapropylammonium hydroxide (TPAOH) as template. Spectral data were processed by factor analysis and MCR chemometric techniques to study the process kinetics and trend in growth, as well as the mechanism of crystallization.

Experimental

Materials and apparatus

The silica source was silica sol (SiO_2, surface area 150-200 m2/g, Rhodia) and aluminium source was aluminium sulphate hydrate (Al_2 $(SO_4)_3$•$18H_2O$) salt (Merck). Sodium hydroxide (NaOH), sulphuric acid (H_2SO_4, 95.0–98.0%) and tetrapropylammonium hydroxide (TPAOH, 40 wt %) were all of analytical grade from Merck. Double distilled deionized water was used in synthesis.

A GNR X-ray diffractometer (Italy) with Cu source was used for structural pattern studies. XRD pattern from 5° to 45° 2θ was recorded at room temperature. As a reference for quantitative assessment of the amount of crystalline obtained nano ZSM-5, the percent crystallinity of each sample was determined from the ratio of height of the most intensive 2θ reflection in the XRD pattern (23.19° 2θ) to the height of the 2θ reflection of the other samples prepared within predetermined time interval of synthesis process [15].

In order to monitor the crystallization process, highly crystalline ZSM-5 sample at the end of seventh days was set as most crystallized condition (100%) and reference sample and all other samples were compared to be scaled according to this. In case of amorphous samples, the intensity of the 23.19° 2θ reflection and the percent crystallinity are zero. An AB-Bomem (Que., Canada) Mid IR spectrometer equipped with a DTGS (D3IB) detector, a KBr Ge/Sb2S3 coated beam splitter and a SiC source was used to record the IR spectra using Spectratech diffuse reflectance cell. Diffuse reflectance spectra were recorded in 4 cm^{-1} resolution with 32 scans over the 400–1000 cm^{-1} spectral region.

Synthesis of nano-zsm-5 zeolite

Nano ZSM-5 was prepared based on the reported procedures [16-18,7]. In the first step a clear solution was prepared with a molar composition of $1SiO_2$: 0.0025 Al_2O_3: 0.07 Na_2O: 0.12 TPAOH: 33 H_2O. The pre-determined amounts of aluminium sulphate hydrate and NaOH were dissolved in a half of predefined water, being aged for 2h by vigorous stirring at room temperature. Then tetrapropylammonium hydroxide was gradually added to obtained solution to obtain a clear solution. The remaining predetermined water and silica sol were mixed in a separate vessel.

Alumina source was added to silica source drop wise during 6h under vigorous stirring at room temperature.

The pH of final solution was adjusted to 10 by sulphuric acid 98%. Obtained gel was transferred to a round-bottomed flask being refluxed for 8 days at 105°C without stirring at atmospheric pressure. During crystallization process as well as mixing stage of initial silica and alumina precursors, gel samples were isolated in predetermined time intervals, being dried at 50 °C for a day and evaluated by mid-IR spectroscopy. For XRD investigation, the product was washed with deionized water and dried at 100°C for 10 h. In order to remove the organic contents, the samples were also calcinated at 550 °C for 6 h.

Chemometric analysis

MCR-ALS is considered a general purpose factor analysis technique which is also applicable for different aims. The recorded mid-IR spectra profiles for synthesis process were arranged into a data matrix D(r×c), where r corresponds to the number of recorded spectra along time and c is referred monitored wavenumbers. MCR methods are based on a bilinear model such as:

$$D = CS^T + E$$

MCR-ALS decomposes the data matrix D into the pure response profiles. The sub-matrices C(r × n), and ST (n × c) are usually associated with the concentration and pure spectral profiles of the resolved components respectively. E is the matrix of residuals not explained by the model and ideally should be close to the experimental error. Before employing the MCR–ALS analysis, factor analysis must be performed to determine the number of effective chemical components (N).

In order to cover purpose singular value decomposition (SVD) [24] and variation in the lack of fit (LOF) for MCR–ALS model were used by adding more components.

MCR model is solved by determining the concentration (C) and pure spectra (S) matrices, utilizing iterative ALS algorithm. The obtained results must optimally fit the experimental data matrix (D). This optimization is carried out for a proposed number of components and using initial estimates of C by different methods like evolving factor analysis (EFA), applying some constraints to model the shapes of the profiles by minimum rotational ambiguity associated with the resolved profiles [20-24].

Non-negativity constraint was used for both concentration and spectral profiles to assume that the concentrations of the species and the intensity of the radiation reflected by the samples in FTIR spectrometric evaluations will always be positive or zero. Unimodality constraint was applied only for the concentration profiles to avoid the presence of more than one peak maximum in the resolved profiles. Closure constraint was hot helpful because of the lack of information about the stoichiometry of the evolving synthesis. EFA and MCR–ALS analysis were performed using available subroutines for MATLAB [12].

Characterization

Field-emission scanning electron microscopy was performed on the samples to determine their particle size and morphology. FE-SEM images of the ZSM-5 crystals were acquired using a Hitachi- 54160 instrument, operating at 2o kV. The data correspond to the diffuse reflectance FTIR spectra was recorded during the synthesis process since initial mixing of reacting agents in 400 - 1000 cm−1 spectral region.

During crystallization at different times, gel products were isolated being evaluated by mid-IR spectroscopy after dehydration. Data acquisition was performed by 1 h time interval during first 2days of initiation of the reaction, followed by 3h intervals at the next 3 days of the reaction, and 2 spectrums in every day for the rest of reaction time. Statistical and chemometric analyses of the data were performed in MATLAB (Mathwork, Inc., version 7- Natick, MA, USA). Spectra from the WINFIRST software were exported in text format being analysed for interpretative aims.

Results and discussion

Figure 1 shows the FE-SEM micrograph of the ZSM-5 synthesized after calcination. Our FE-SEM study revealed that the particles present in the prepared samples have a uniform distribution and their morphologies are regular and spherical shape. The average particle sizes of the zeolite samples, estimated based on the FE-SEM pictures are in 50-100 nm range. Figure 2 shows the FTIR spectral variations of solid product of ZSM-5 synthesis along reaction time.

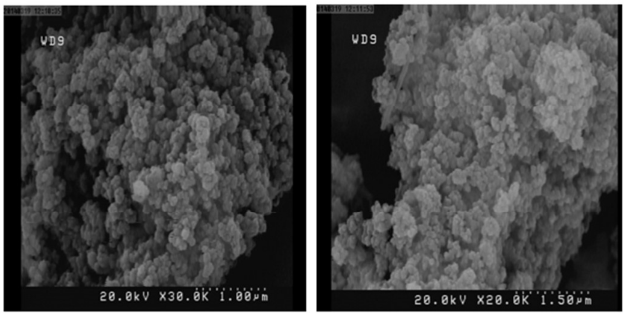


Fig. 1. SEM images of synthesized nano ZSM-5.

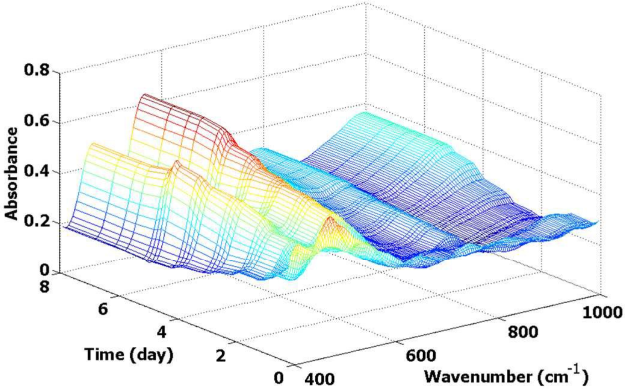


Fig. 2. FTIR spectra recorded along the reaction and changes in the absorbance spectra of solid product of ZSM-5 nanocrystals through evolution in different time intervals.

Pure silica is in amorphous structure phase and absorption bands at ~460 and ~800 cm-1 correspond to Si-O bending vibrations and Si-O-Si symmetric stretching modes [25]. Infrared spectra of pure ZSM-5 show spectral features at 792, 546 and 453cm−1 corresponding to TO4 (T = Si, Al) symmetric stretching, stretching mode of structural silicate double-ring units and Si-O bending vibrations, respectively [26-27].

The signal appeared at 550-560 cm-l region indicates the formation of ZSM-5 and is not observed in amorphous silica sources which would be hydrolysed in the presence of sodium hydroxide [15]. Silicate does usually exist as polymerized-state polysilicate in strongly basic solution as well as aluminosilicate ions via condensation reaction with aluminate. These polysilicate or aluminosilicate ions are depolymerized upon heating of the synthesis mixture to reorganize of the silicate oligomers which is followed by formation of inorganic-organic composite species [28]. The availability of soluble silicate influences the rate at which these composite species inorganic-organic are formed and the formation of composite species that then provide the fundamental units for nucleation and crystal growth of zeolite is the key step of the crystallization .Van der Waals contacts are established between the hydrophobic silicate species and TPA molecules in inorganic-organic composite species.

At first, signal intensity would increase in the 450 – 500 cm^{-1} region, which is probably related to the initial formation of polymerized-state polysilicates and the hydrated aluminosilicate gel in strongly basic solution. Decreasing and broadening of signal intensity in the region between 450 - 550 cm-1 can be seen slowly due to depolymerization of silica upon heating of synthesis mixture [15, 28-29]. Till at the second day of reflux little signal splite begins to occur within 450-550 cm^{-1} range which becomes intensive along the progress of crystallization process. Improvement in the absorbance intensity 550 cm-1 signal corresponds to the increased concentration of ZSM-5 nano crystals in the reaction gel solution.

The advantage of factor analysis and MCR methods was utilized in processing the overlapped absorption profiles of the synthesis gel solution in order to determine the kinetics of nano particle formation evolution.

Achieving the initial estimate of the number of independent species which are present through the evolutionary process is a significant step for the MCR–ALS analysis.

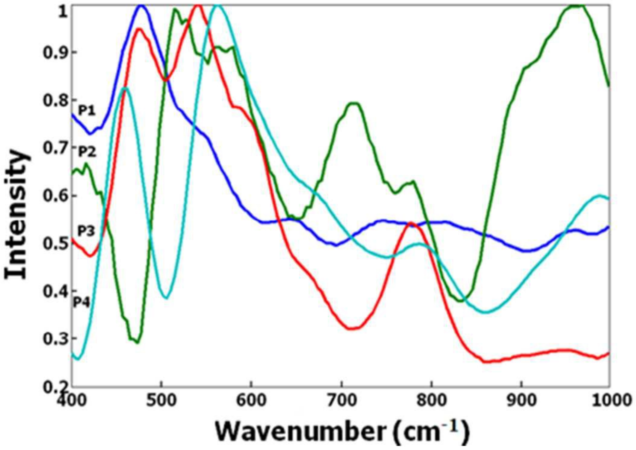
Factor analysis was used to determine the number of independent species possessing distinguished by the spectral characteristics [10, 30].

Table 1 shows the results of the absorbance data matrices of growth process presented to SVD. In this table, the eigenvalues (EV), the logarithm of the eigenvalue (log EV), the corresponding eigenvalue ratio, and the cumulative percent of variances of the explained (CPV) are presented. The acquired data from factor analysis of growth progress spectra demonstrated that the first four principal components would cover noticeable systematic variances.

Table 1. The results of usage factor analysis on the absorbance data matrix of evolution process

Factor no.	EV	Log EV	CPV	EVR
1	622.365099	6.433527	98.1640	
2	9.072796	2.205280	99.5950	0.0146
3	1.722183	0.543593	99.8666	0.1898
4	0.485127	-0.723345	99.9431	0.2817
5	0.189747	-1.662059	99.9730	0.3911
6	0.111777	-2.191249	99.9906	0.5891

EV, eigenvalues; Log EV, logarithm of the eigenvalue; CPV, cumulative percent of variances; EVR, eigenvalue ratio



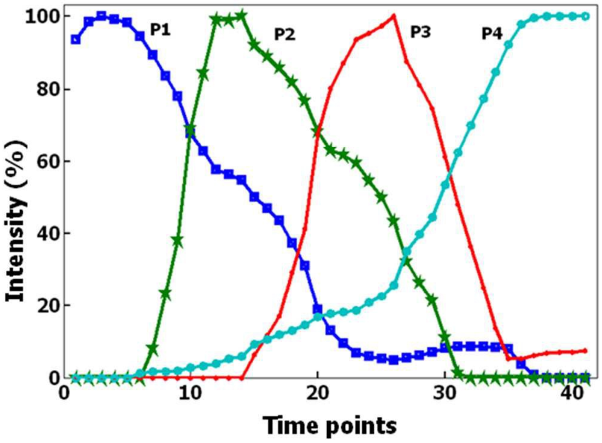


Fig. 3. Concentration profiles and normalized pure spectra of the resolved by MCR–ALS for ZSM-5 nanoparticles evolution during reaction

According to CPV, the first four factors could explain more than 99.9% of variances in the spectroscopic data set and the rest may be due to noise.

Another one is the root mean square of differences between the spectral forms calculated by the MCR-ALS model and those reproduced by FA. The respective obtaining LOF values at convergence were 3.21 and 2.15 and the resulting MCR-ALS model could reproduce 99.9% of variances in the experimental data. Figure 3 shows the concentration profiles and normalized pure spectra of the resolved components for the reaction, determined by the MCR–ALS analysis. As it can be seen from concentration profiles, the corresponding concentration of the P1 specie would increase initially and being followed by a definite decrement along the process together with the appearance of the P2 specie. According to the reaction mechanism P1 specie related to the initial formation of polymerized-state polysilicates and the hydrated aluminosilicate gel in strongly basic solution. By dissolving these polymeric and aluminosilicate structures upon heating of the synthesis mixture, concentration of the P1 specie is decreased. The routes by which zeolite crystals are produced from an amorphous aluminosilicate or silica source are complicated self-assembly processes involving multiple simultaneous and related equilibria and condensation steps [15]. Figure 4 demonstrates the schematic evolution of the proposed mechanism of synthesis and chemical structures representing spectral components [28,29].

The conventional mechanism proposed for zeolite crystallization is commonly understood as a solution mediated process with two main steps: nucleation (formation of the first and very small crystalline entities) and crystal growth around these nuclei [28-29, 31]. Synthesis process of a zeolite consists of two steps: the initial formation of the hydrated aluminosilicate gel being followed by the gel crystallization.

P2 species are probably related to formation of inorganic-organic composite species between the hydrophobic silicate species and TPA template molecules as Grieken et al [31] have called “particulate material” by amorphous primary particles.

P3 specie also according to literature [31] has attributed to secondary particles which is created from aggregation of primary particles and is larger units.

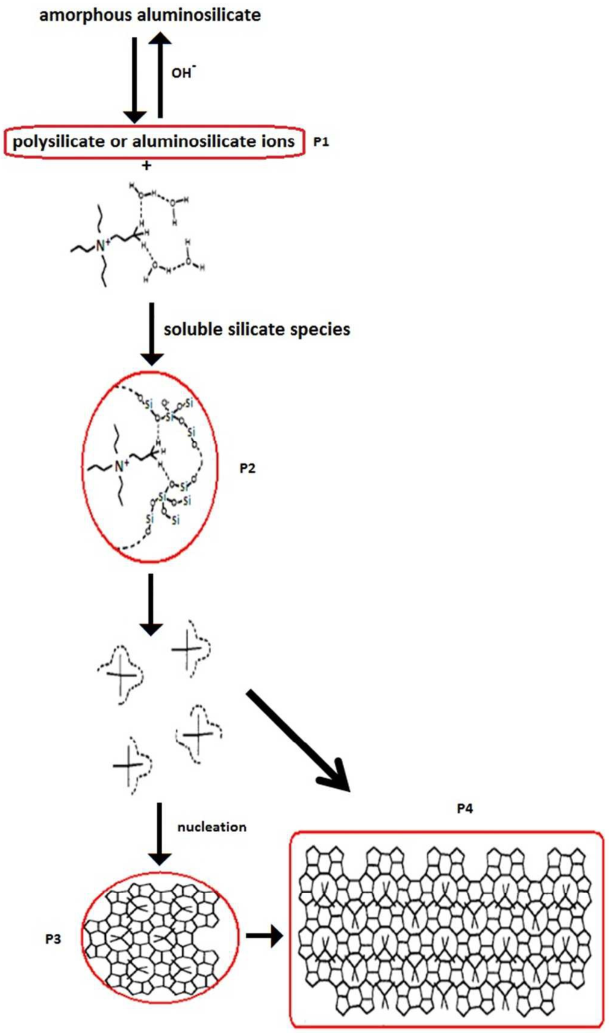


Fig. 4. Scheme for evolution of the proposed mechanism of synthesis

Finally, the secondary particles are gradually transformed into nanocrystalline ZSM-5 crystals through a zeolitization process and p4 species are probably related to these particles [31].

P4 concentration profiles during the crystallization process of zeolites and the composition of the hydrogel are similar to pure ZSM-5 and its relative intensity could be related to amount of crystal. The obtained crystallinity results by XRD (Fig. 5) as mentioned in experimental section in comparison with amount of ZSM-5 acquired by DRIFT is presented in Table 2. Obtained results confirm reasonable agreement between two methods.

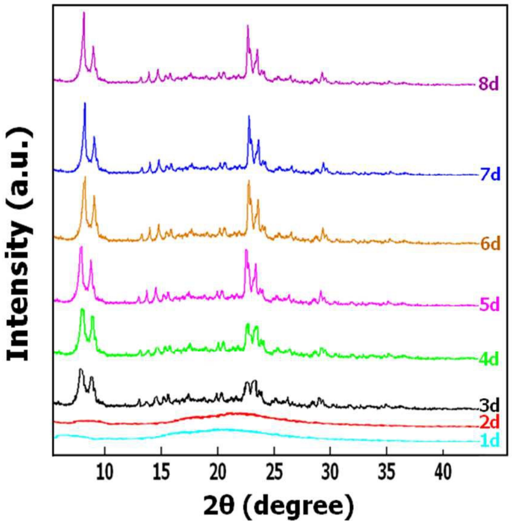


Fig. 5. XRD spectra of as-synthesized samples obtained in different days.

Table 2. The obtained crystallinity results by XRD and DRIFT

Time (day)	Crystallinity %	
	XRD	DRIFT
1	0	0
2	0	3
3	35	26
4	50	53
5	90	85
6	96	98
7	100	100
8	99	101

Sample	X_{XRD}	X_{DRIFT}	d_i	sing	rank	Signed rank
1	0	0	0	ND	ND	ND
2	0	3	-3	-	3.5	-3.5
3	35	26	9	+	6	+6
4	50	53	-3	-	3.5	-3.5
5	90	85	5	+	5	+5
6	96	98	-2	-	1.5	-1.5
7	100	100	0	ND	ND	ND
8	99	101	-2	-	1.5	-1.5

Another route to consider the coincidence between two series of data obtained by XRD and DRIFT methods is to employ non-parametric or distribution-free method [32]. Box and whisker plots (also known as box plots) are visual outputs which represent the comparative situation of both analytical methods (Fig. 6). These plots indicated that the two groups characterized by a skewed distribution and also the spread (defined by the box length) for the evaluated cases is similar which reveals that the within laboratory precision is the same.

The Wilcoxon signed rank test (also known as Wilcoxon t-test) was applied for two paired samples in order to evaluate whether there is a significant difference between the results of the methods. A two-sided (two tailed) test was performed and results obtained for DRIFT (XDRIFT) were compared with those of XRD reference method (XXRD).

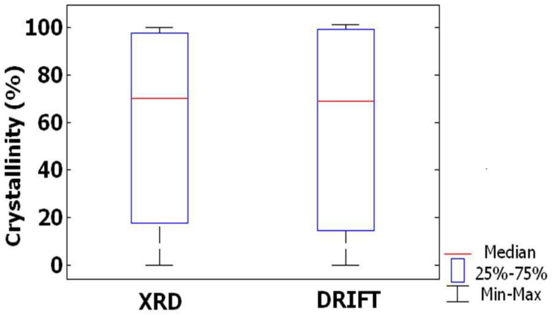


Fig. 6. Box and whisker plots used in the comparison crystallinity (%) in two Techniques XRD and DRIFT

Illustrating outcome of Wilcoxon signed rank test for two paired samples is presented in Table 3. In case of each sample, the sign of the difference between XXRD and XDRIFT is considered. Differences equal to zero have not been taken into account since they have no sign. The absolute values of di, the differences for each pair of measurements were ranked. Regarding repeated observations (ties) mean of the ranks was replaced. As an example here value -2 as well as -3 have occurred twice; they were both given (1+2)/2 = 1.5 and (3+4)/2 = 3.5 rank. Afterwards each rank was attributed the same sign as the original difference. If there was no true difference between the two paired samples there should not be a large difference between the sum of positive ranks (T^+) and that of negative ones (T^-). The test consists in comparing r = min (T^+, T^-) to a critical value. Null hypothesis is rejected if the calculated T is less or equal to the tabulated T. It is noticeable that in parametric tests the null hypothesis is rejected if the calculated test-statistic is larger than the tabulated critical value. In this work the critical value for two tailed test of significance at $\alpha = 0.05$ and n = 8, was 3, $T^+ = 11$, $T^- = 10$ and therefore r=10. Thus the null hypothesis was accepted and that there was no significant difference between the results of the methods.

The conclusions section should come in this section at the end of the article, before the acknowledgements.

Table 3. Data to illustrate the Wilcoxon signed rank test for two paired samples XXRD and XDRIFT

Conclusions

In this work, nano ZSM-5 was prepared through reflux crystallization method. FA and MCR–ALS methods were utilized to process DRIFT spectral data, obtained from monitoring the synthesis process in different process times, in order to gain insight the mechanism and kinetics of zsm-5 formation evolution. Chemometric analysis was the mean to study the evolution mechanism of the nano ZSM-5 formation through monitoring their DRIFT absorption spectra. This chemical mechanism for changes in all species in various solution conditions was interpreted by the MCR–ALS. The results presented here confirm the reported mechanisms for ZSM-5 growth. The obtained results can suggest new spectroscopic method for assessment of crystallization in fabrication of nano structures.

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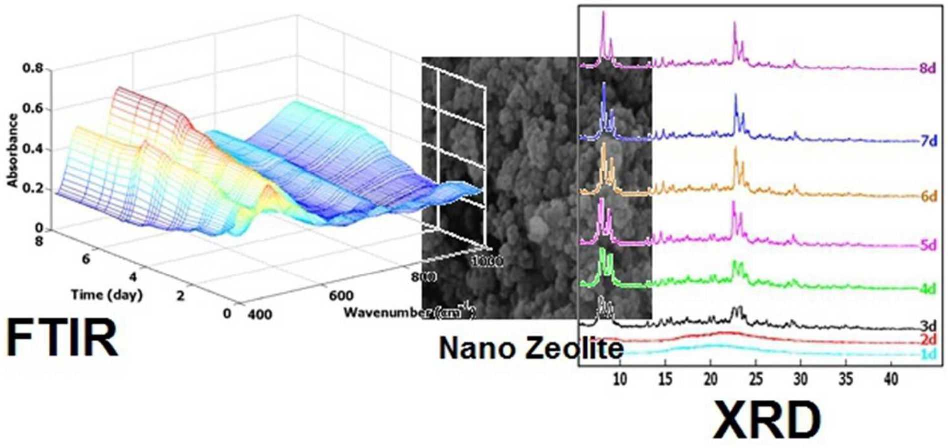

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