

Ultrasound-assisted dealumination of zeolite Y

M HOSSEINI, M A ZANJANCHI*, B GHALAMI-CHOOBAR and H GOLMOJDEH

Department of Chemistry, Faculty of Science, University of Guilan, P. O. Box 1914, Rasht, Iran
e-mail: zanjanchi@guilan.ac.ir

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Abstract. We demonstrate a new procedure for dealumination of zeolite Y. The method employs a 28 KHz ultrasound bath and an ethanolic acetylacetone solution. Acetylacetone was used as chelating agent and ultrasound irradiation was used as extraction intensifier. Four types of samples, as-synthesized, ammonium-exchanged, acidic and neutralized zeolite were used for dealumination. Parts of the framework aluminum atoms are removed from their sites in the structure of zeolite Y upon the use of either acetylacetone on its own or simultaneous use of acetylacetone and ultrasound waves. Higher dealumination was observed for those samples subjected to both ultrasound irradiation and acetylacetone extraction.

Keywords. Microporous; zeolite Y; dealumination; ultrasound irradiation; extraction.

1. Introduction

Zeolite Y is one of the most famous and versatile catalysts in both research purposes and also industrial applications.^{1–3} Zeolite Y can be converted to acidic zeolites to be active in many catalytic reactions.⁴ In zeolite Y the Si/Al molar ratio plays an important role in solid acidity, catalytic activity and also the porosity of material. Zeolites with higher Si/Al ratios are more active in some catalytic reactions including catalytic cracking reactions.⁵

The framework of zeolite Y is based on sodalite cages that are joined by O-bridges between the hexagonal faces.⁶ Eight sodalite cages are linked forming a large central cavity or supercage, with a diameter of about 12 Å. The supercages share a 12-membered ring with an open diameter of 7.4 Å. Zeolite Y is synthesized with low Si/Al ratio, i.e., between 2.5 and 2.9 and they cannot be synthesized directly as a high-silica form.⁷ As the ratio of Si/Al in zeolite Y is a very crucial parameter affecting its catalytic activities, various approaches were thought to convert it to the zeolite with higher Si/Al ratio. Therefore, in many cases it is necessary to implement a method to remove parts of the framework aluminum atoms for a desirable catalytic application. Also, decreasing the aluminum content of the zeolite is usually a desirable trend to produce more stable zeolite with higher silica content. According to the literature, dealumination which is the removal of framework aluminum atoms without harshly disrupting the crystalline structure of zeolites, is an important process. In this

process some of the Si–O–Al bonds are broken and extra-framework aluminum atoms are formed.⁸ The synergetic interaction between Brönsted acid sites (originated from framework aluminum atoms) and Lewis acid sites (originated from extra-framework aluminum atoms), increases the efficiency of the dealuminated zeolite for the catalytic reactions.⁹

Steaming, SiCl₄ treatment, leaching with hydrochloric acid and reaction with chelating agents such as acetylacetone, ammonium hexafluorosilicate, and oxalic acid are some of the post-synthesis methods used for dealumination of zeolites.¹⁰ These methods often require high temperature conditions or need a flow-type tube reactor. Also applying leaching or chelating treatments usually require long times. Therefore, these techniques are relatively inconvenient.

In recent years, sonication has been reported as a complementary means to carry on some reaction processes in the field of zeolite preparation or modification^{11–14} The chemical effects of ultrasound waves are attributed to the phenomenon of the cavitation.¹⁵ This effect generates many tiny bubbles in liquid media and mechanical erosion of solids, including particle cracking. Therefore, sonication provides an efficient contact between the solid and the extractant. Reports are also available on ultrasonic wave assisted synthesis of various metal nanoparticles.^{16,17}

Acetylacetone is a suitable chelating agent for extraction of aluminum from zeolites. It extracts them as Al(acac)₃ complexes and these complexes can be washed out of the zeolite crystals.¹⁸ In this study, we investigated the effect of sonication on the extraction of the aluminum atoms from their sites in zeolite Y. We

*For correspondence

used acetylacetone as chelating agent. To the best of our knowledge there is no published report on the application of ultrasound waves and acetylacetone extraction procedure for dealumination of zeolites.

2. Experimental

2.1 Materials and methods

Silica powder (Degusa, Switzerland), $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ (Fluka No. 6421), NaOH (Merck No. 106462), NH_4Cl (Merck No. 101145), HCl (Merck No. 100317), acetylacetone (Merck No. 800023), ethanol (Merck No. 111727), benzaldehyde (Merck No. 801756), beta-naphtol (Merck No. 822290) and aluminum powder (Merck No. 820052) were used without further purification.

Preparation of zeolite Y was based on our previously published report.¹⁹ The ammonium form of the zeolite was prepared upon conventional ion-exchange treatment using an aqueous solution of 0.4 M NH_4Cl at 25°C for 24 h. The obtained solution was filtered and the zeolite was washed with deionized hot water for several times and dried at 110°C. To convert the ammonium form of the zeolite to acidic one, it was heated in a muffle furnace at rate of 10°C/min and holding at 550°C for 5 h. Also, the neutralized form of HY zeolite was prepared by neutralizing the acidic form using solution of 0.1M NaOH. The initial, ammonium-exchanged, acidic and neutralized forms of the zeolites are designated as Y, NH_4Y , HY and NaY, respectively.

In a typical extraction treatment about 1g of each of the four types of zeolite Y were added to 3 mL of a solution of acetylacetone in ethanol (38%) separately. The samples were left in contact with stirred acetylacetone solution for 2 h. During this time the container was capped to prevent evaporation of the mixture. After that,

samples were washed with 10 mL ethanol at 60°C and dried at room temperature in a stream of dry air. These samples are designated with “acac” at the end of their represented symbols (table 1).

All the processes described above for the extraction treatment were repeated, but in the presence of ultrasound waves. An ultrasonic bath (SAIRAN, 7500S) with a power of 600 W and frequency of 28 KHz was used. For the purpose of sonication, zeolite samples in ethanolic acetylacetone were irradiated with ultrasound waves for 30 min. We found this time by performing the experiments at various times. A higher dealumination could be attained at longer ultrasound irradiation. However, we found that longer than 30 min. exposure time leads to little damage of the zeolite structure (as evidenced by examining the XRD patterns). These treated samples were designated with an extension of “acac(us)” at the end of their referred symbols.

The aluminum content of the zeolite samples was determined using electron microprobe X-ray analysis (EMPA) We also calculated aluminum content of the solid samples based on X-ray diffraction data. This calculation is based on Dempsey *et al.* data.²⁰ According to their report there is a linear correlation between the lattice parameter (cell constant) and the Si/Al ratio in zeolite Y samples.

As a probe reaction, synthesis of a xanthenes derivative (14-phenyl-14*H*-dibenzo[*a, j*]) which requires an acidic catalyst, was chosen to investigate the effect of altering Si/Al molar ratio of the zeolites before and after sonication treatments. For this purpose, a mixture of β -naphtol (0.42g, 2 mmol), benzaldehyde (1mmol) and catalyst (20 mg) was stirred in an oil-bath (100°C) under solvent-free conditions. After completion of the reaction (monitored by TLC) the product was cooled to room temperature. Ethanol (5 mL) was added to it and filtered to separate the catalyst. Then the crude collected solid was recrystallized to give the pure product.²¹

Table 1. Designation, textural properties and Si/Al ratios of the prepared zeolites.

Sample designation	Surface area (m ² /g)	Pore Volume (cm ³ /g)	Si/Al Ratio	
			XRD calculation	EMPA analysis
Y	745	0.265	2.68	2.58
Y-acac	635	0.226	2.84	2.78
Y-acac(us)	580	0.206	3.2	2.82
NH_4Y	605	0.220	2.83	2.81
$\text{NH}_4\text{Y-acac}$	590	0.210	2.87	2.85
$\text{NH}_4\text{Y-acac(us)}$	583	0.207	3.67	3.1
HY	579	0.206	2.97	2.74
HY-acac	536	0.191	3.10	3.49
HY-acac(us)	491	0.174	4.04	3.7
NaY	552	0.185	3.03	2.82
NaY-acac	504	0.179	3.51	3.61
NaY-acac(us)	426	0.150	4.67	4.48

2.2 Characterization

A Philips PW1840 X-ray diffractometer with Cu K α radiation was used to record the powder XRD patterns. The BET specific surface area of the samples was determined by nitrogen adsorption at liquid nitrogen temperature on a Sibata SA-1100 surface area analyzer. Microprobe analysis (EMPA) was accomplished by a VEGA-TESCAN scanning electron microscopy. Scanning electron microscopy (SEM) was used to study morphology of the zeolites. The SEM micrographs were recorded by a Leo-1430VP microscope.

3. Results and Discussion

3.1 Si/Al variation

All the prepared materials and their designations are shown in table 1. Specific surface area, pore volume, Si/Al molar ratios acquired from the two different

methods is listed in table 1. All the symbols used for designation of the prepared samples were defined in the Experimental section.

X-ray diffraction patterns of the prepared zeolites, before and after the extraction treatments, are shown in figure 1. The parent, acac-treated and ultrasound-assisted acac-treated samples are designated by a, b and c, respectively. The characteristic diffraction peaks for the zeoliteY are confirmed by comparing the XRD data with those reported in the standard reference source and JCPDS No. 00-038-0240.²² The main XRD reflections for zeoliteY appear at around $2\theta = 6.27^\circ$, 10.20° , 11.95° , 15.71° , 18.74° , 20.40° , 23.68° and 27.07° (attributed to (111), (220), (311), (331), (333), (440), (533), and (642) crystal planes respectively). The XRD patterns for all the acac-treated and ultrasound-assisted acac-treated samples are similar to the diffraction pattern of the parent zeolite. Therefore, the structural integrity was satisfactorily retained after dealumination. Figure 1 shows that the intensity

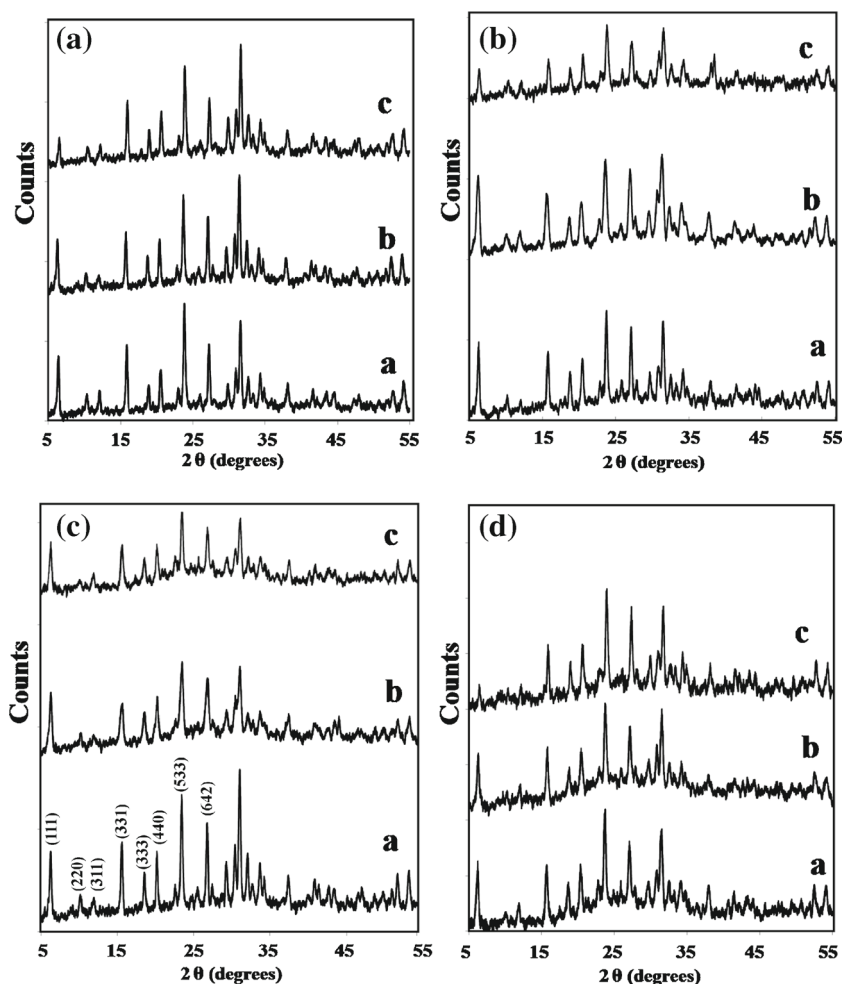


Figure 1. XRD patterns of the prepared zeolites: A (Y), B (NH₄Y), C (HY) and D (NaY). (a), (b) and (c) are referring to the parent, acac-treated and ultrasound-assisted acac-treated zeolites, respectively.

of the diffraction peaks of the treated samples were slightly decreased due to the extraction treatment. It is not wise to evaluate the degree of crystallinity of our treated and dealuminated zeolites by direct comparison of the peak heights in XRD patterns because the final products don't have the same composition as the parent zeolite.^{23,24}

Figure 2 shows variation of the unit cell size due to the extraction treatments. The results show that application of ultrasound waves caused more reduction in the unit cell size. Gradual contraction of the unit cell size is an indication of higher dealumination of the zeolite samples.

The SEM micrographs in figure 3 show a uniform morphology almost identical for all the prepared samples before and after ultrasonic treatment. They exhibit an average size of 300–500 nm. It is interesting to note that upon different treatment, the crystallites preserve their morphology and do not crack.

The surface area and pore volume were calculated using the data of the liquid nitrogen physisorption experiments. As it is evident from table 1, surface area values for the initial and successive altered zeolites show a gradually decreasing trend. The decrease can be due to some structural damages and possible pore destructions imposed by each steps of the chemical treatments (ammonium-exchange, calcination, neutralization). It can be deduced that under current experimental conditions, the prepared samples have the surface area values in order of: $Y > NH_4Y > HY > NaY$. The same trend was also observed for the acac-treated or ultrasound-assisted acac-treated zeolites. Part of the decrease in pore volume and surface area for these samples may be attributed to the formation of larger

pores when aluminum atoms are extracted from the framework, as suggested by Jones *et al.*²⁵

Table 1 shows the Si/Al ratios calculated from both EMPA and XRD data for all the samples. There is clear evidence that the Si/Al are increasing more upon simultaneous exploitation of acac-treatment and ultrasound irradiation for dealumination of Y, NH_4Y , HY and NaY samples. This indicates that ultrasound waves affect dealumination in a positive way. Also, shorter times are needed for dealumination of the zeolite samples in the presence of ultrasound waves. The increased Si/Al ratio due to acac treatments (in the presence or absence of ultrasound waves) is not within the same order for the different types of our Y, NH_4Y , HY and NaY zeolites. It seems that consecutive treatments to convert the zeolite to its ammonium, acidic and neutralized forms cause successively higher dealumination.

It is noticeable that the Si/Al values are not similar when comparing the results obtained from EMPA analysis with those obtained from X-ray diffraction data for the same sample. Table 2 compares the percent of dealumination in the absence and in the presence of ultrasound waves for the different forms of our zeolite Y evaluated from EMPA and XRD data. The table shows that there is inconsistency among the results obtained from EMPA analysis in comparison with those obtained from XRD data. The increase in dealumination due to sonication (last column in table 2) which were achieved from XRD data are higher for all the samples. An explanation to this discrepancy may be issued based on the type of aluminum atoms that are involved in the calculation. This is related to the difference between framework and extra-framework aluminum. Parts of the aluminum atoms which are removed from their tetrahedral sites may still remain in the lattice occupying extra-framework or non-framework sites.^{26–28} These are measured by EMPA. But the method which calculates Si/Al ratios from crystallographic parameter (cell constant) accounts for framework aluminum only.

3.2 Activity demonstration

Synthesis of a xanthenes derivative was chosen as a reaction model for comparing catalytic activity of the parent and dealuminated zeolite Y samples. Scheme 1 shows the specific reaction pathway for the synthesis of 14-phenyl-14*H*-dibenzo[*a, j*] xanthene. Our heterogeneous catalytic system is composed of the mixture of the aldehyde and the β -naphthol containing the solid acidic zeolite. The yield and/or reaction time could be considered as the appropriate parameters for evaluating the effectiveness of the catalysts. As table 3 shows, the higher yield and lower reaction time was obtained

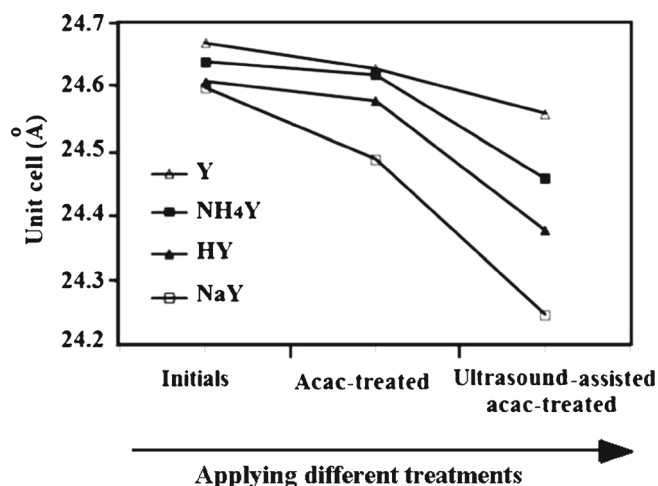


Figure 2. Calculated unit cell dimensions for the initials, acac-treated, and ultrasound-assisted acac-treated zeolite Y samples from XRD data.

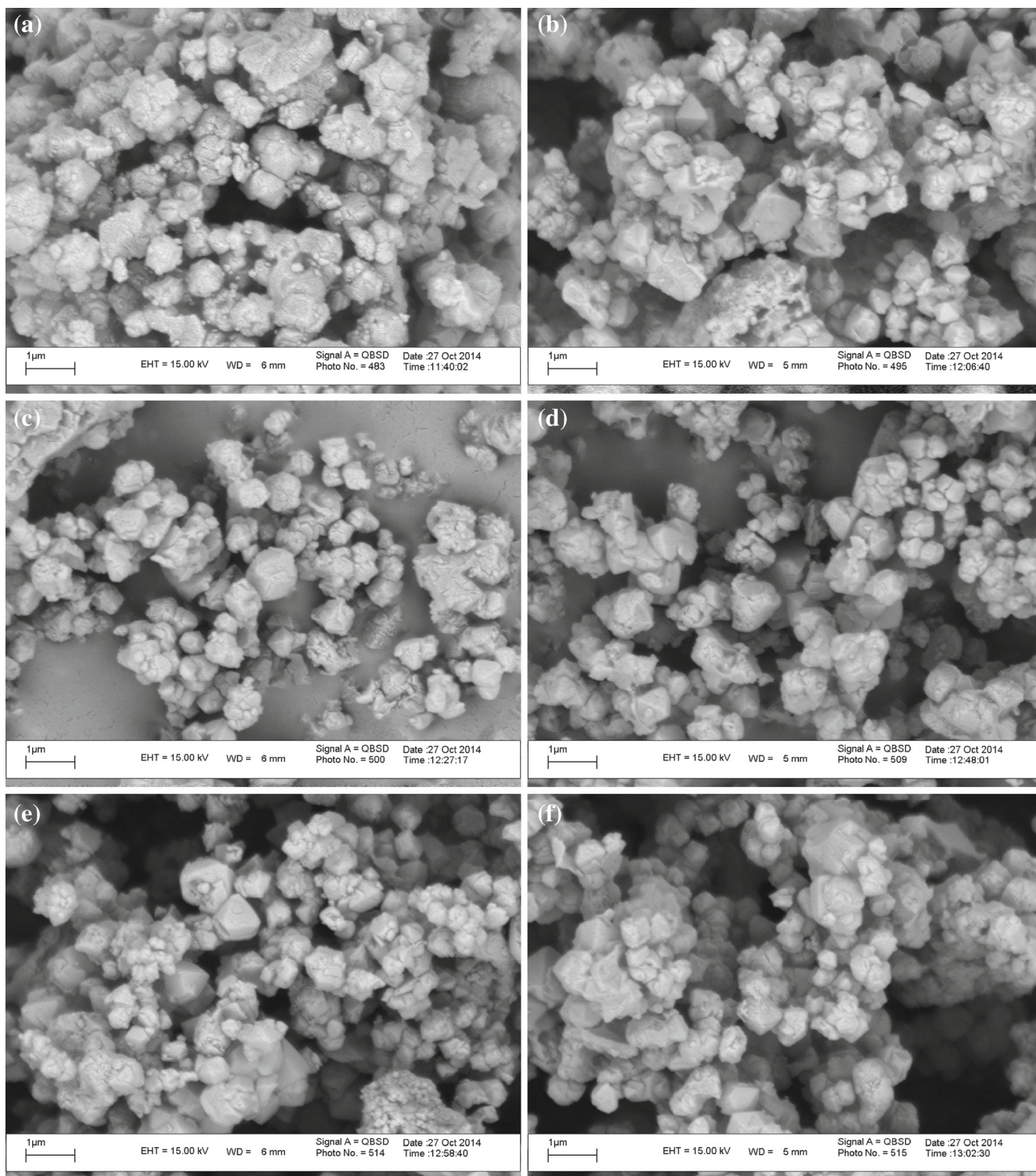


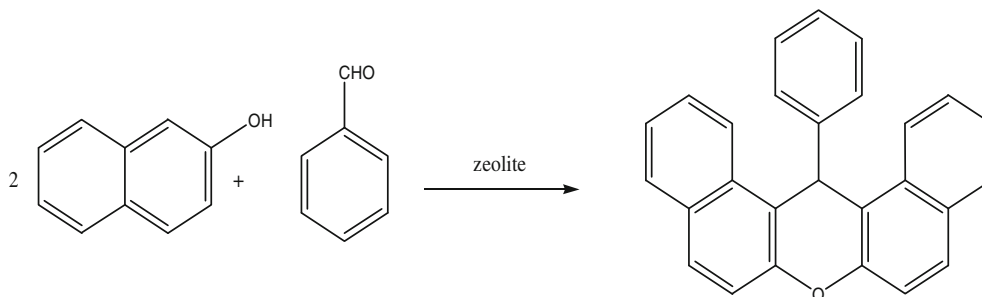
Figure 3. SEM micrographs recorded for prepared zeolites: A: Y, B: NH₄Y-acac, C: HY-acac, D: HY-acac(us), E: NaY-acac and F: NaY-acac(us).

using HY-acac(us) catalyst. This is the most dealuminated zeolite Y among the three HY ($\text{Si}/\text{Al} = 2.97$), HY-acac ($\text{Si}/\text{Al} = 3.10$) and HY-acac(us) ($\text{Si}/\text{Al} = 4.04$) tested acidic catalysts. This clearly shows that the

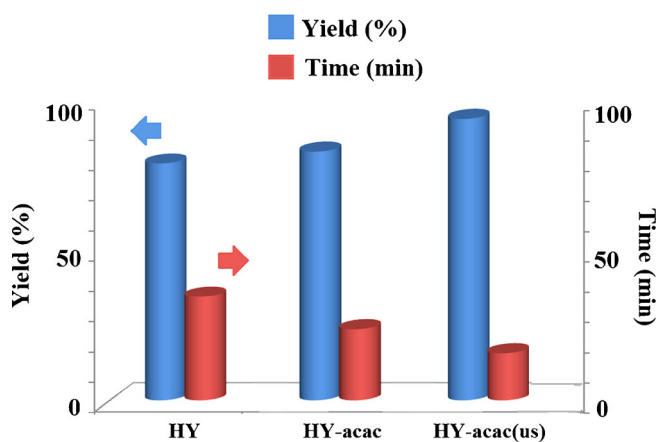
acidity and activity of this catalyst is higher for the catalyst with higher Si/Al ratio (higher dealumination). The pictorial results presented in figure 4 also show better performance of this catalyst.

Table 2. Percent of dealumination due to the treatments in absence and presence of ultrasound waves based on EMPA and XRD analysis.

Sample	Type of Analysis	Acac-treatment	Acac-treatment in presence of US	Increase (%)
NH4Y	EMPA	7.1	12.0	4.9
	XRD	5.0	21.2	16.2
HY	EMPA	20.1	24.1	4.0
	XRD	10.3	27.0	16.7
NaY	EMPA	22.4	34.7	12.3
	XRD	18.4	35.1	16.7

**Scheme 1.** Reaction pathway for synthesis of 14-phenyl-14H-dibenzo[*a, j*] xanthene.**Table 3.** Acquired yields for synthesis of the xanthenes using the parent, acac-treated and ultrasound-assisted acac-treated HY catalysts.

Sample	Yield (%)	Reaction time (min)
HY	80	35
HY-acac	84	24
HY-acac(us)	95	16

**Figure 4.** Observed reaction time and yield for synthesis of 14-phenyl-14H-dibenzo[*a, j*] xanthene using different HY catalysts.

3.3 Mechanism

The mechanism of dealumination of zeolites upon the use of acetylacetone is related to the chelating property

of this compound. The acetylacetone molecule as a bidentate ligand can extract parts of the aluminum atoms from their sites in the structure of the zeolite and hence accomplish dealumination. The progress of dealumination of our zeolite samples in the presence of ultrasound waves indicates that sonication can intensify this extraction process. The mechanism of this intensification could be attributed to the efficient contact between the zeolite particles and the chelating molecules. The ultrasound waves generate cavitation and mechanical erosion of the solid which in turn improve the efficacy of the extraction. This feature has also been claimed while ultrasound waves were used for the extraction of contaminants in food and environmental samples.¹⁵

4. Conclusion

Our results show that sonication in combination with acac-treatment has considerably increased the dealumination of zeolite Y. Dealumination progressively increases Si/Al ratio especially in HY and NaY zeolite samples. The method of EMPA provided Si/Al ratios taking into account the total aluminum (framework and extra-framework) remained in the structure of zeolite Y. Also, crystallographic calculations, based on the XRD data, gave Si/Al ratios taking into account framework aluminum atoms only. This new method allows fast and convenient dealumination of zeolite under simple conditions and within a very short period of time.

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References

- Martinez C and Corma A 2011 *Coordin. Chem. Rev.* **255** 1558
- Bejblova M, Zilkova N and Cejka J 2008 *Res. Chem. Intermed.* **34** 439
- Bellussi G and Pollesel P 2005 *Stud. Surf. Sci. Catal.* **158** 1201
- Beyerlein R A, Chio-feng C, Huggins J B and Ray G J 1997 *Top. Catal.* **4** 27
- Almutairi M T, Mezari B, Filonenko G A, Magusin P, Rigutto M S, Pidko E A and Hensen E 2013 *Chem-CatChem* **5** 452
- Baerlocher C, McCusker L B and Olson D H 2007 In *Atlas of zeolites framework types* 6th Ed. (Amsterdam: Elsevier)
- Rüscher C H, Salman N, Buhl J and Lutz W 2006 *Micropor. Mesopor. Mater.* **92** 309
- Dimitrijevic R, Lutz W and Ritzmann A 2006 *J. Phys. Chem. Solids* **67** 1741
- Biaglow A I, Parrillo D J, Kokotailo G T and Gorte R J 1994 *J. Catal.* **148** 213
- Karge H G and Weitkamp J (Eds.) 2002 In *Molecular Sieves: Science and Technology* (Berlin: Springer) Ch 3
- Erten-Kaya Y and Cakicioglu-Ozkan F 2012 *Ultrason. Sonochem.* **19** 701
- Wang B, Wu J, Yuan Z Y, Li N and Xiang S 2008 *Ultrason. Sonochem.* **15** 334
- Jabariyan Sh and Zanjanchi M A 2012 *Ultrason. Sonochem.* **19** 1087
- Shu S, Husain Sh and Koros W 2007 *Ind. Eng. Chem. Res.* **46** 767
- Tadeo J L, Sánchez-Brunete C, Albero B and García-Valcárcel A I 2010 *J. Chromatogr. A* **121** 72415
- Wani I A and Ahmad T 2013 *Colloid Surf. B* **101** 162
- Wani I A, Ganguly A, Ahmed J and Ahmad T 2011 *Mater. Lett.* **65** 520
- Zanjanchi M A and Razavi A 2001 *Spectrochim. Acta A* **57** 119
- Zanjanchi M A, Tabatabaeian K and Moosavifar M 2001 *J. Inclu. Phenom.* **40** 193
- Dempsey E, Kuhl G H and Olson D H 1969 *J. Phys. Chem.* **73** 387
- Shirini F, Abedini M and Pourhasan R 2013 *Dyes Pigments* **99** 250
- Treacy M M J and Higgins J B 2001 In *Collection of Simulated XRD Powder Patterns for Zeolites*, 4th Ed., (Elsevier: Amsterdam)
- Rakoczy R and Traa Y 2003 *Micropor. Mesopor. Mater.* **60** 69
- Anderson M and Klinowski J 1986 *J. Chem. Soc. London Faraday Trans.* **82** 1449
- Jones Ch, Hwang S, Okubo T and Davis M 2001 *Chem. Mater.* **13** 1041
- Xu B, Bordiga S, Prins R and van Bokhoven J A 2007 *Appl. Catal. A* **333** 245
- Siantar D P, Millman W S and Fripiat J J 1995 *Zeolites* **15** 556
- van Bokhoven J A, Roest A L, Koningsberger D C, Miller J T, Nachttegaal G H and Kentgens A P M 2000 *J. Phys. Chem. B* **104** 6743