APPENDIX

APPENDIX

Adsorption of wintergreen and eucalyptus essential oil on zeolites

Introduction

Essential oils (EO) are obtained from aromatic plants as secondary metabolites and characterized by their intense aroma. They have a wide range of applications due to their aromatic properties, such as perfumes, aromatherapy, health care, personal care products, and food preservation (Bakkali et al., 2008). However, essential oils are known to exhibit high volatility, leading to a reduced perception of their odor over time. Therefore, it is important to maintain the odor characteristics of essential oils for longer by encapsulating EO in porous materials.

Zeolites are crystalline aluminosilicates interconnected by corner-sharing $[SiO_4]_4^-$ and $[AlO_4]_5^-$. The framework contains different pore sizes, shapes and hydrophobic or hydrophilic properties. These unique characteristics of zeolites have led to various applications as catalysts, ion exchangers, and adsorbents (Tekin and Bac, 2016). Moreover, they have low toxicity, low cost and stable structure. Zeolite can be used as host materials for EO encapsulation and controlled release.

Researchers have tried to encapsulate fragrance molecules in porous materials such as cyclodextrin and metal-organic frameworks (MOFs). However, the major limitations of cyclodextrin and MOFs are high cost and toxicity. Then, an alternative way to encapsulate fragrances in porous material for controlled release of fragrance, such as zeolite. Costa et al. (2022) studied the encapsulation of different fragrances using two zeolite structures (FAU and MOR). The retention of fragrances in zeolite increased in the order NaX<NaY and NaMOR for cinnamaldehyde, limonene, methyl anthranilate, and vanillin. Tekin et al. (2015) encapsulated triplal using zeolite X with different average particle diameters (20 μm and 4 μm). The larger particles show a

slower release of triplal. Therefore, the properties of pore structure, crystal size, and chemical composition of zeolites have an influence on the adsorption and release behavior of fragrances. The interest in this work is encapsulated essential oils in different zeolite structures (NaA and NaX), Si/Al ratios (NaX and NaY), and crystal sizes for prolonged fragrance release.

Research objectives

1. To synthesize essential oils encapsulated in zeolites with difference structures, Si/Al ratios for long time release of essential oils.
2. To understand the adsorption and release behavior of fragrance from zeolites.

Literature review

Essential oils

Essential oil (EO) is a volatile fragrant that is extracted from plant material through the process of steam distillation. Several EOs exhibit highly promising biological applications, as they are non-toxic at very low concentrations (Ríos, 2016). They are commonly used in various products, including perfumes, personal care items, food preservation, and healthcare.

Methyl salicylate is the major constituent found in wintergreen oil, which is obtained through the distillation of wintergreen leaves. It possesses analgesic properties and is commonly utilized in analgesic creams or gels intended for topical application. The effects of methyl salicylate are multifaceted, exhibiting analgesic, anti-inflammatory, and counterirritant properties (Dasgupta et al., 2014).

The oil of eucalyptus is extracted through distillation from the fresh leaves of different Eucalyptus species. It is a colorless or pale-yellow liquid with a distinct aroma and camphoraceous odor. When tasted, it has a pungent, camphor-like flavor that is followed by a cooling sensation. Eucalyptus oil is widely used for relieving symptoms associated with nasopharyngeal infections. It can be consumed internally in the form of mixtures or inhaled for its therapeutic benefits (Evans and Evans, 2009).

As essential oil compounds are highly volatile, encapsulating them within porous materials provides the capability to control the release of the molecules and protect them from evaporation.

Encapsulation of fragrances in porous material

Porous materials are a class of substances characterized by the presence of voids or pores within their structure. Examples of such materials include cyclodextrin, metal-organic frameworks (MOFs), silica nanoparticles, activated carbon, and zeolites. These materials have found widespread application as support or carriers for the controlled release of various fragrances. They exhibit good storage, high porosity, and greater adsorbability, which depends upon the properties of pore structure, molecular structure, and the interaction of fragrance molecules with porous materials.

Metal–organic frameworks (MOFs) are porous materials that have become a prominent category of crystalline materials characterized by their exceptional porosity, reaching up to 90% free volume, and vast internal surface areas that exceed 6,000 m^2/g. These properties, MOFs have found a wide range applications in industrial fields such as gas adsorption, heterogeneous catalysis, and controlled release of fragrances.

Cyclodextrins are macrocyclic compounds with a truncated cone-like structure formed by linking oligosaccharides through α-1,4-glucosidic bonds. These cyclodextrins, often abbreviated as CDs, are extensively utilized in host-guest chemistry for encapsulating target molecules within their cavities. The use of cyclodextrin complexes as controlled release systems has enabled their application in various biocompatible domains, encompassing functional foods and drug delivery. Moreover, this capability has paved the way for their use in encapsulating and releasing flavors and fragrances, preserving the product's original organoleptic properties for consumers.

B. Zhang et al. (2019) reported the encapsulation of fragrances in γ-cyclodextrin (γ-CD)-based MOFs for controlled release of fragrances. In comparison to γ-CD and γ-CD-MOFs, the γ-CD-MOF showed higher encapsulation capability and prolonged fragrance release due to the enhanced host–guest hydrophobic and hydrogen bonding interactions of their porous structures.

However, the major limitations of MOFs and cyclodextrin are toxicity and high cost. Therefore, an alternative way to encapsulate fragrances in porous material for control of the release rate of scents is zeolite. Zeolite is a candidate for prolonged fragrance release because it is non-toxic, low-cost, and considered green.

Encapsulation of fragrances in zeolites

Zeolites are crystalline aluminosilicates containing pores and cavities. The primary structural units of zeolites are the tetrahedra of silicon and aluminum. They are applied for catalysis, ion exchange, and adsorption. The differences in the structure, morphology, hydrophobic/hydrophilic properties, pore size, crystal size, and chemical composition of zeolites have an influence on the adsorption ability of essential oils. Zeolites LTA and FAU structures, including NaA, NaX, and NaY, are interesting in this work. NaX and NaY zeolites have the same FAU structure but differ in their Si/Al ratios. Specifically, NaX has a Si/Al ratio of 1-1.5, while NaY has a Si/Al ratio greater than 1.5.

Table A1 shows examples of encapsulation of fragrances in porous materials. Eucalyptus essential oil can be encapsulated in zeolites Y covalently with **β**-cyclodextrins. The results in the table showed that the synthesized zeolites exhibited superior efficiency in encapsulating eucalyptus essential oil compared to free **β**-cyclodextrins. Additionally, they were effective in reducing the release kinetics of the oil.

Table A1 Example of encapsulation of fragrances in porous materials.

Materials	Fragrance (FG)	Result	Ref.
Natural zeolite (Micro 20) and synthesis molecular sieve (MSU-S)	Citral, p-cymene, geraniol, menthol	MSU-S is a better adsorbent of FG than micro-20.	Strzemiecka et al. (2012)

Table A1 (Continued) Example of encapsulation of fragrances in porous materials.

Materials	Fragrance (FG)	Result	Ref.
NaX	Triplal	Larger particles have lower desorption rates.	Tekin et al. (2015)
Recyclable porous material (RPMs)	Ethyl butyrate (EB) and D-limonene (DL)	FG release rates: EB@RPM (1 h) > DL@RPM (1.5 h)	Vaughn et al. (2013)
NaY	D-limonene	Fast release in 2 weeks	Costa et al. (2022)
NaX	Cinnamaldehyde	Fast release in 2 weeks	
NaY	Methyl anthranilate	Release at longer time (720 days)	
NaMOR	Vanillin	Release at longer time (720 days)	
NaYCDsuc NaYCDadi NaYCDcit	Eucalyptus essential oil (EEO)	Modified zeolites reduced the release of EEO more efficiently than free EEO	Mallard et al. (2018)
Rice husk	Methyl salicylate (MS)	Rice husk (RH) bio sorbents from agricultural waste had the potential to release MS slowly for delayed ripening in Namwa bananas.	Cholmaitri et al. (2020)

In this work, essential oils will be encapsulated in zeolites with different structures, including NaA, NaX, and NaY zeolites. The synthesized zeolites and encapsulated essential oils in zeolites was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), Fourier transform infrared spectrometry (FTIR), and N_2 adsorption analysis.

Research procedure

Chemicals and materials

Chemicals for synthesis NaA, NaX, and micron NaY zeolites are fumed silica (99.8% SiO_2, Sigma-Aldrich), sodium aluminate (41.383% Na_2O, 58.604% Al_2O_3, Riedel-de Haën®), and sodium hydroxide (97%wt NaOH, Carlo-Erba). The chemical for the preparation of solution B of nano NaY is Ludox® HS-40 colloidal silica (40%wt silica suspension in H_2O).

Synthesis of zeolite NaA by using fumed silica as a silica source

Synthesis of zeolite NaA, NaX, NaY

Zeolite NaA was synthesized with the same gel ratio and procedure as in Section 3.12, 3.13, and 3.14. Fumed silica was used as a silica source.

Material characterization

The synthesized zeolites were characterized by XRD, FTIR, SEM-EDS, and N_2 adsorption-desorption analysis as reported in Section 3.2.

Results and Discussion

Characterization of zeolite NaA

Figure A1 shows the XRD patterns of the synthesized zeolite. The characteristic XRD peaks of zeolite NaA appear at $2\theta \sim 7°$, 10 and $\sim 12°$. These peaks are narrow and sharp, indicating the high crystallinity and purity of the product.

FTIR spectra of zeolite NaA (Figure A2) shows characteristic zeolite bands related to zeolite structures. The band at 460 cm^{-1} indicating Si-O bending vibration of Si-O-Si, at 550 cm^{-1} indicating Si-O stretching vibration of Si-O-Si, at 660 cm^{-1} indicating Si-O stretching vibration of O-Si-O, at 1000 cm^{-1} indicating O-Al-O asymmetry stretch vibration, at 1600 cm^{-1} indicating Si-OH bending vibration, and at 3400 cm^{-1} indicating -OH stretch vibration of Si-OH.

Figure A3 presents the SEM images of synthesized zeolite NaA, showing cubic morphology of 0.2-1 μm. Its Si/Al ratio was 1.04.

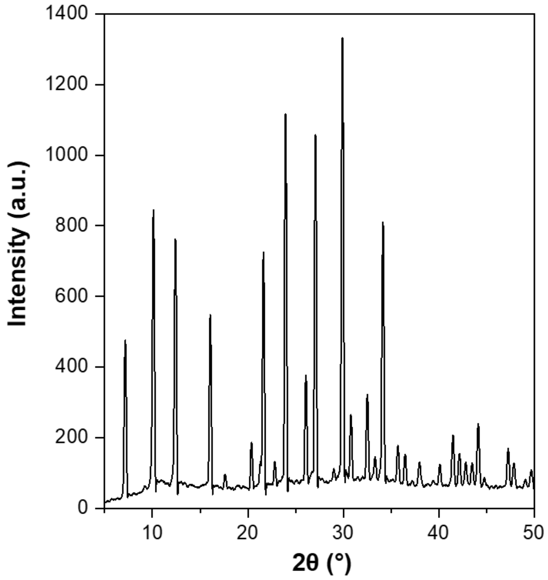

Figure A1 The XRD pattern of zeolite NaA.

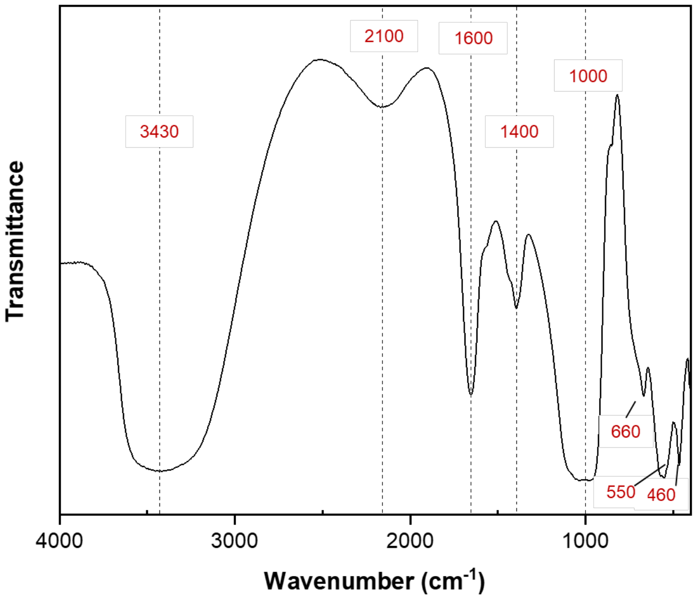

Figure A2 FTIR spectra of zeolite NaA.

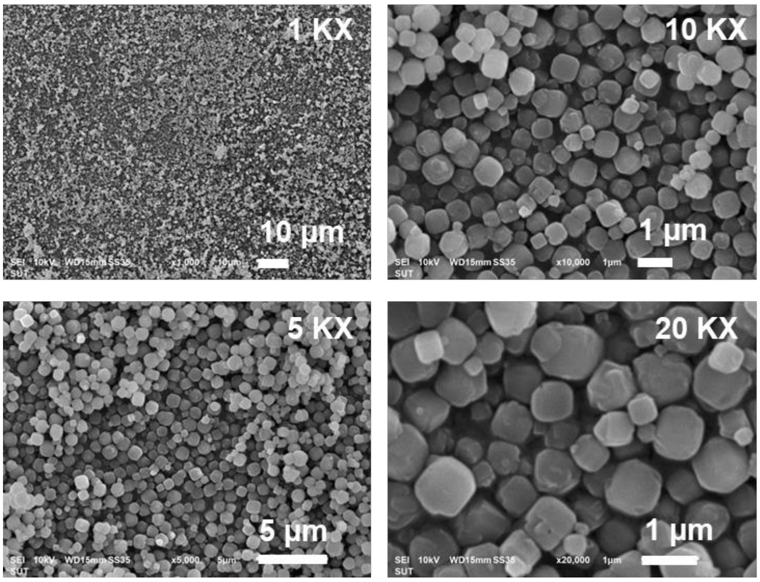

Figure A3 SEM images of zeolite NaA with a magnification of 1, 5, 10 and 20 KX.

Characterization of zeolite NaX

Figure A4 shows the XRD patterns of the synthesized zeolite NaX showing the FAU characteristic peaks. Its FTIR spectra (Figure A5) shows the band of Si-O-Si bending at 444 cm^{-1}, Si-O-Si stretching at 675 cm^{-1}, O-Si-O stretching at 746 cm^{-1}, O-Al-O asymmetric stretching at 1000 cm^{-1}, Si-OH bending at 1648 cm^{-1}, Si-OH stretch at 3433 cm^{-1}. The SEM image (Figure A6) confirmed the non-uniform polycrystal morphology of zeolite NaX with Si/Al ratio 1.33.

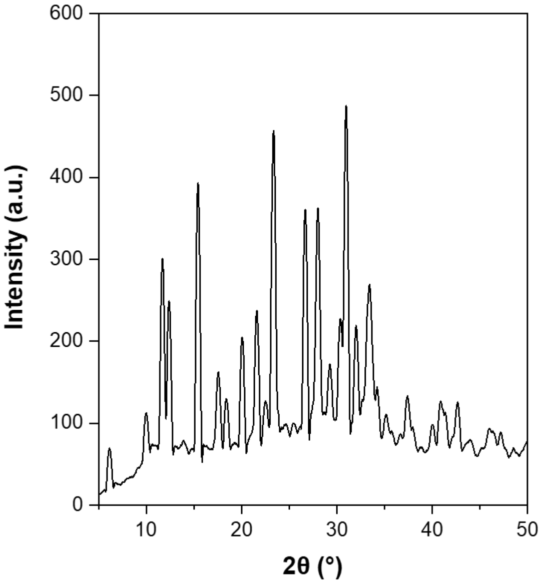

Figure A4 The XRD pattern of zeolite NaX by using fumed silica as silica source.

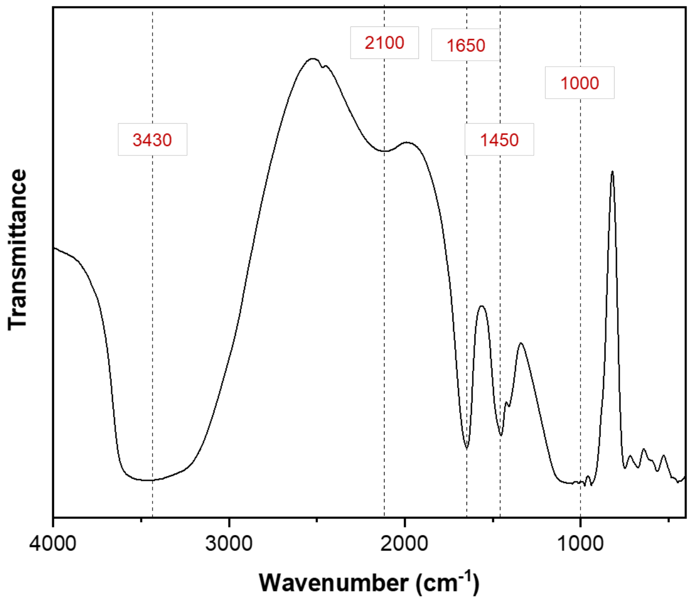

Figure A5 FTIR spectra of zeolite NaX by using fumed silica as silica source.

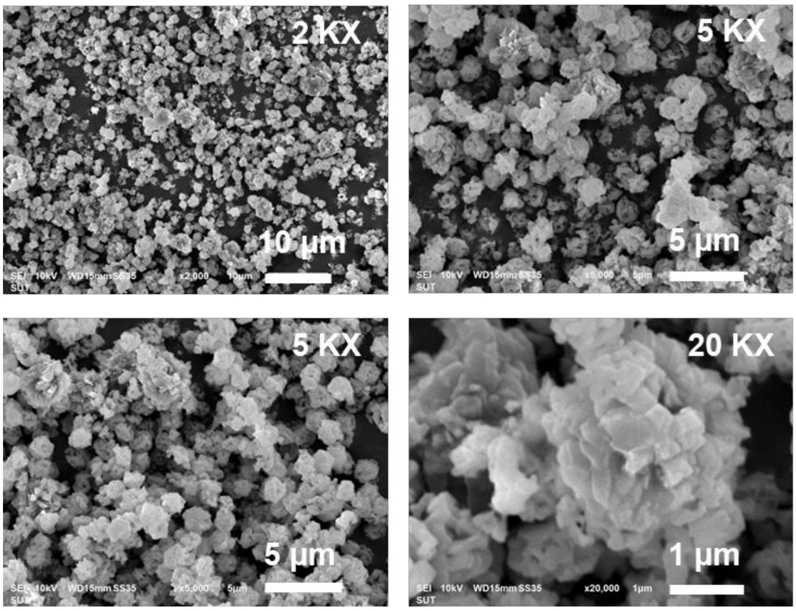

Figure A6 SEM images of zeolite NaX by using fumed silica as silica source with a magnification of 2, 5 and 20 KX.

Characterization of zeolite NaY

Figure A7 shows the XRD pattern of pure-phase zeolite NaY with sharp peaks, consistent with most of the reports on the diffraction peaks at $2\theta \sim 6°$, 10 and ~ 15°. Figure A8 shows its FTIR spectra with bands at 450 cm^{-1} (Si-O-Si bending), at 572 cm^{-1}

(Si-O-Si stretching), at 699 cm^{-1} (O-Si-O stretching), at 1030 cm^{-1} (O-Al-O asymmetric stretching), at 1644 cm^{-1} (O-Si-OH bending), at 3466 cm^{-1} (Si-OH stretching). This sample presents an agglomerate of polyhedral morphology with Si/Al ratio 2.19 (Figure A9).

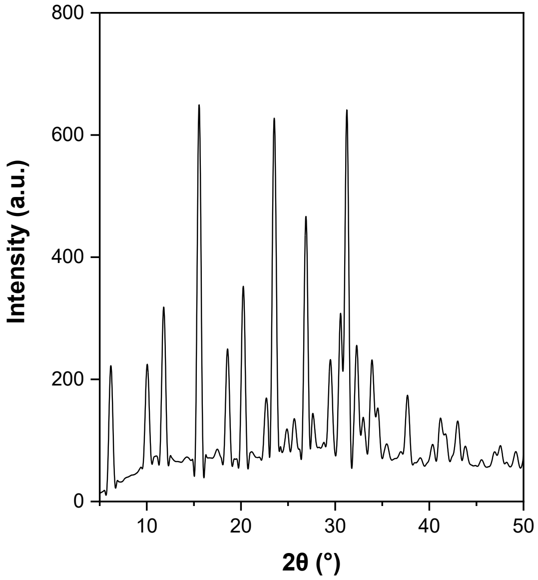

Figure A7 The XRD pattern of zeolite NaY by using fumed silica as silica source.

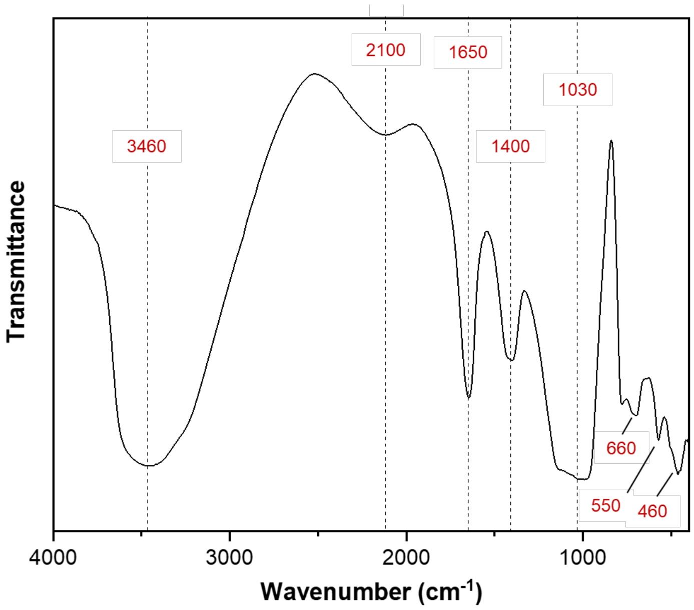

Figure A8 FTIR spectra of zeolite NaY by using fumed silica as silica source.

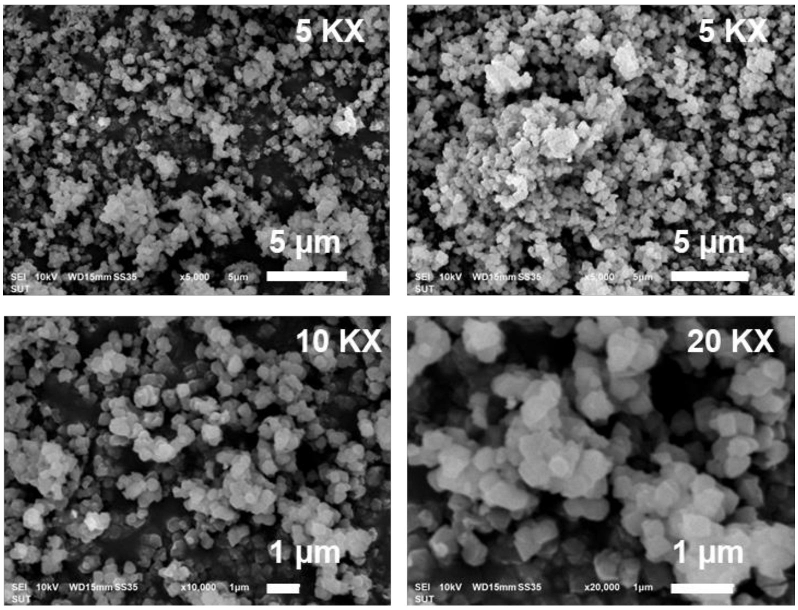

Figure A9 SEM images of zeolite NaY by using fumed silica as silica source with a magnification of 5, 10 and 20 KX.

Preparation of encapsulated essential oils (EO) in zeolites

The encapsulation of essential oils was conducted with the procedure from Costa et al. (2022). Samples were prepared by dissolving 0.4 mmol essential oils in 10 mL of ethanol and adding to 1.5 g of NaA, NaX, micron NaY zeolites, respectively. Fragrance encapsulation was performed by adding solutions with zeolites in a 125 mL PP bottle and allowing it to stir (300 rpm) for 72 h at room temperature (25±5 °C). After that, the samples was centrifuged at 4000 rpm for 3 min and dried EO/zeolites at 40 °C for 72 h to remove the ethanol. Then, the supernatant solutions and EO/zeolites was stored in glass flasks sealed with parafilm and placed in a refrigerator to prevent evaporation and maintain a closed system.

Release fragrance from zeolites

The encapsulated methyl salicylate (MS) in zeolites was stored in vials sealed with parafilm, and these were placed in desiccators at room temperature (24±5 °C). The methyl salicylate release experiments were carried out at room temperature during 0-5 h. The amount of essential oils from zeolites and the release profiles was monitored using the thermogravimetric (TGA) analysis. The TGA was performed by

Mettler Toledo model TGA/DSC1 in N_2 gas with a flow rate of 50 mL/min at a heating rate of 10 ˚C/min up to 350 ˚C.

The TGA profiles of all the adsorption methyl salicylate in synthesized zeolites samples (Figure A10-A13) show two regions of weight loss. The first is attributed to the desorption of water in the zeolite structure (80-250 ˚C). The second attributed to the decomposition of methyl salicylate at 100-220 ˚C. Therefore, this result cannot determine the amount of methyl salicylate in zeolites because the peak of water overlaps with a peak of methyl salicylate.

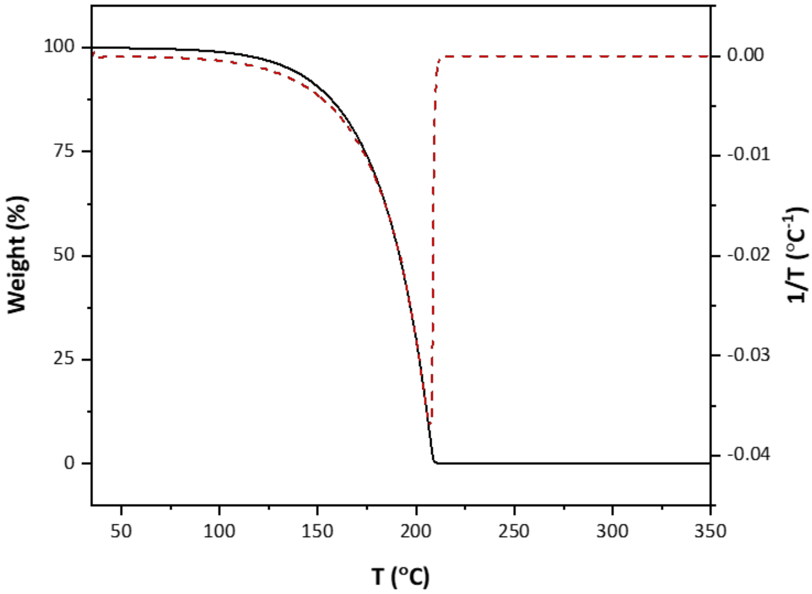

Figure A10 TGA curve of liquid methyl salicylate.

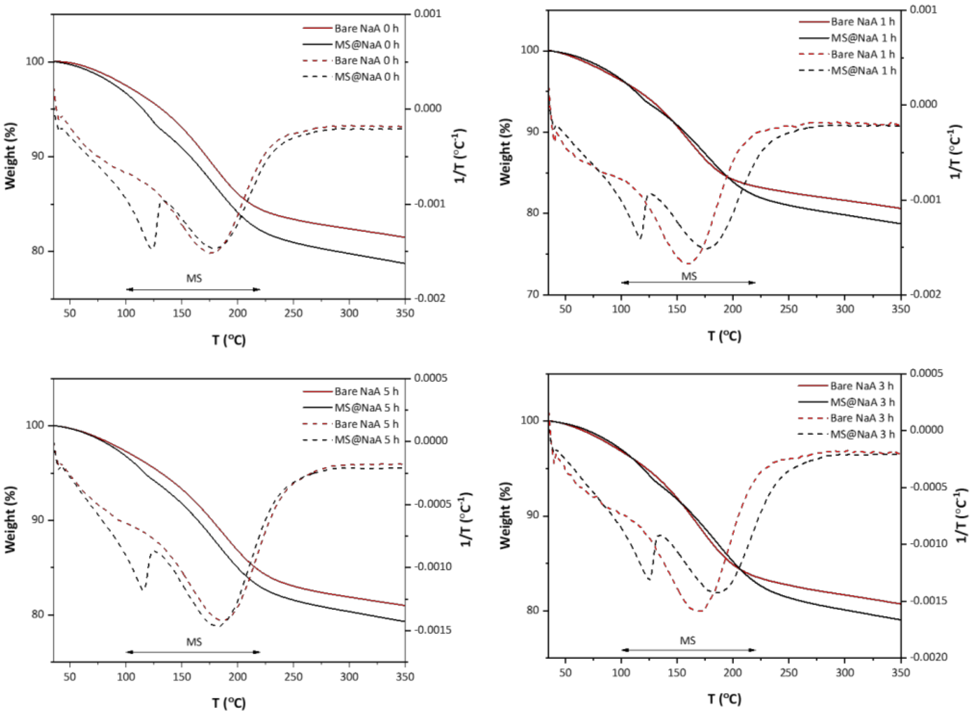

Figure A11 TGA curve of MS@NaA and bare NaA (time = 0, 1, 3 and 5 h).

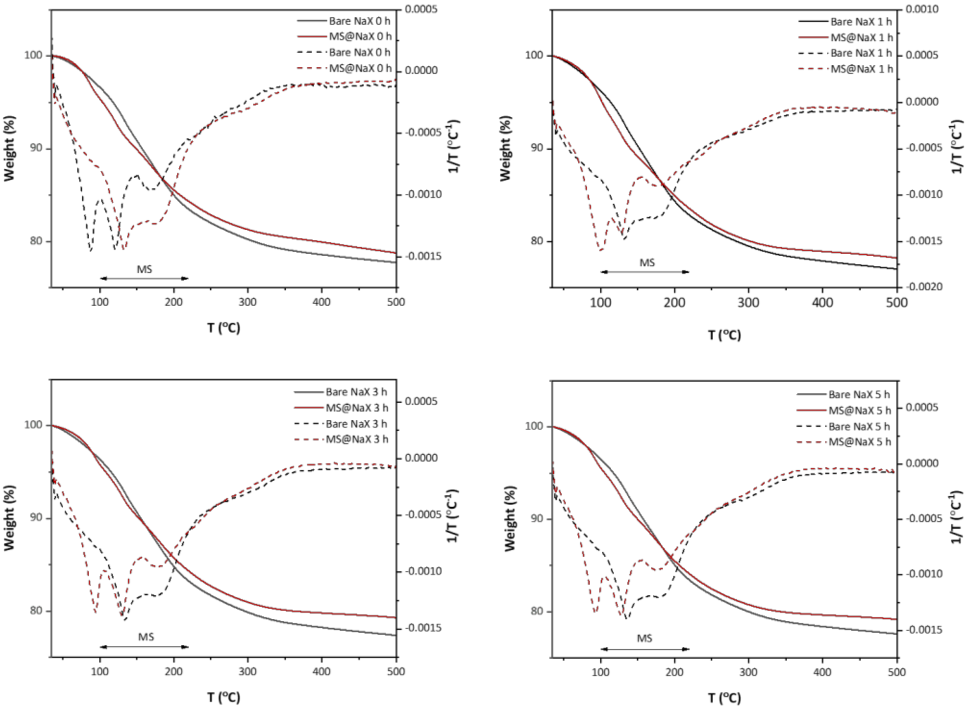

Figure A12 TGA curve of MS@NaX and bare NaX (time = 0, 1, 3 and 5 h).

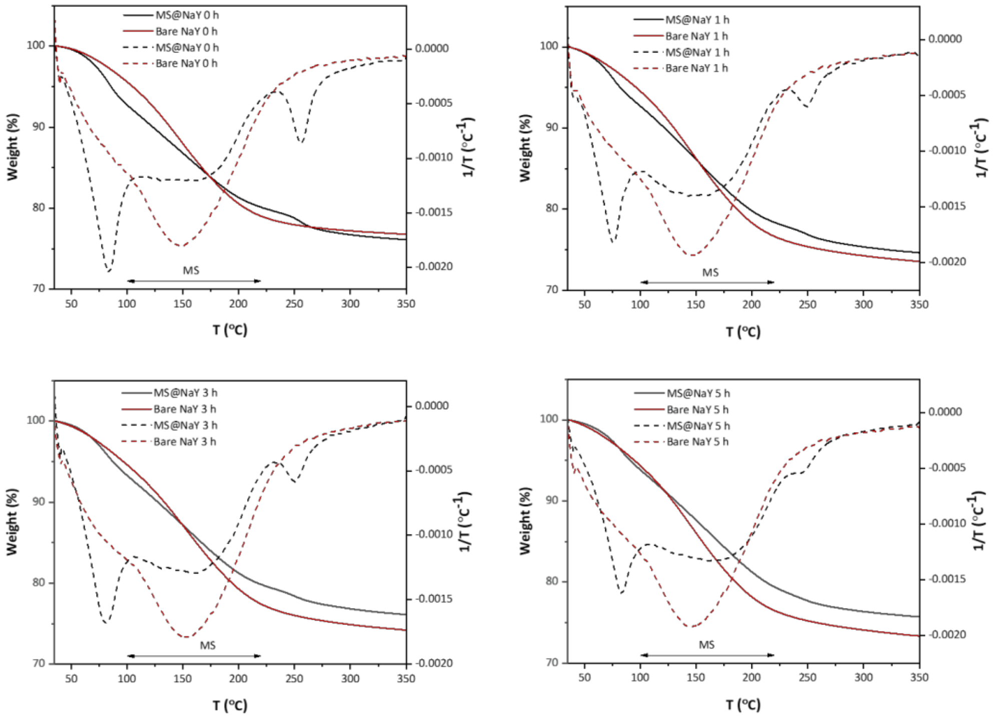

Figure A13 TGA curve of MS@NaY and bare NaY (time = 0, 1, 3 and 5 h).

Adsorption of methyl salicylate in zeolites by solid-gas adsorption

At the beginning of the temperature-programmed experiment (pre-heat zeolite), 0.1 g of zeolite powder was put into the tube, and then the tube was heated by tube furnace at 200 °C for 2 h with N_2 gas was introduced into the tube. After the temperature of the furnace had cooled down to room temperature, the power of the furnace was shut off while the N_2 was continued in the experiment.

The liquid of methyl salicylate was heated at 120 °C in an oil bath, and N_2 gas was passed through a gas bubbler containing essential oils to introduce essential oils vapor into the zeolites at room temperature for 1, 3, and 6 h. Figure A14 shows a Diagram of the adsorption of methyl salicylate in zeolites by solid-gas adsorption.

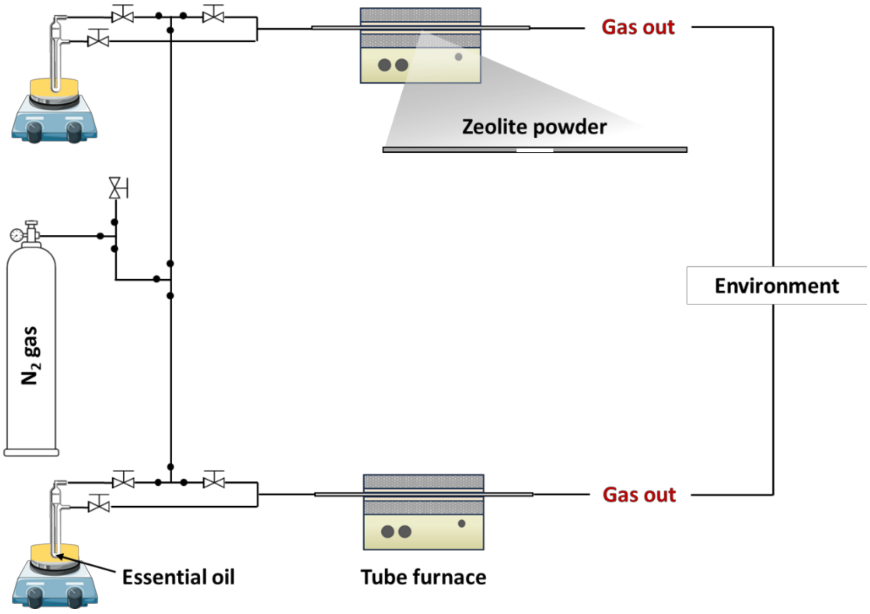

Figure A14 Diagram of adsorption essential oils in zeolites by solid-gas adsorption.

Determine the amount of methyl salicylate in zeolites by GC-FID

The amount of methyl salicylate in zeolite was analyzed by Gas chromatography-flame ionization detection (GC-FID). Heated zones were set at 220 °C for injection and detector port. The initial oven temperature was 80°C and was maintained for 4 min. It was then heated at 10°C/min to 220 °C and held for 3 min. All samples were injected manually at a volume of 1 μL.

Preparation of standard solutions

Standard solutions of methyl salicylate 5 mL were prepared by dissolving it in ethanol at concentrations 250, 500, 1000, 1500, 2000, 3000, and 4000 ppm. Nitrobenzene 40 μL used as the internal standard for methyl salicylate. Figure A15 shows the calibration curve of standard solutions.

Preparation of sample solutions

Sample solutions were prepared by dissolving 2 mL of ethanol in a 20 mL vial and stirring at 100 ± 5 °C for 24 hours to extract methyl salicylate from the zeolite for GC analysis. The samples were then filtered using a 0.22 μm syringe filter.

Next, 1000 µL of the filtrate and 40 µL of nitrobenzene were transferred into a 10 mL volumetric flask. The flask was then filled with ethanol up to the calibration mark to prepare the solution for methyl salicylate determination in zeolites.

Figures A16-A24 show the adsorption of methyl salicylate in synthesized zeolites in different adsorption times. The retention times of ethanol (solvent) and nitrobenzene (internal standard) were 0.2 and 3 min, respectively. The peak of methyl salicylate was not observed in all samples. These results show that methyl salicylate cannot access zeolites.

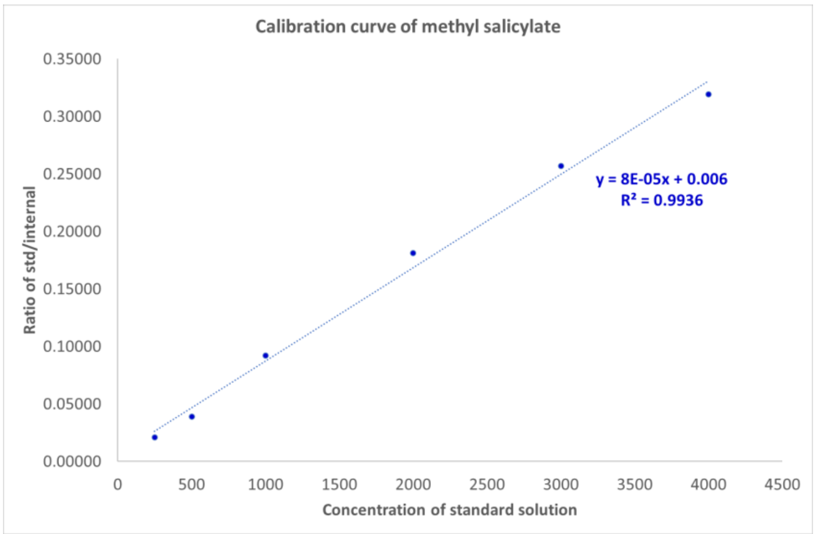

Figure A15 Calibration curve of standard solutions.

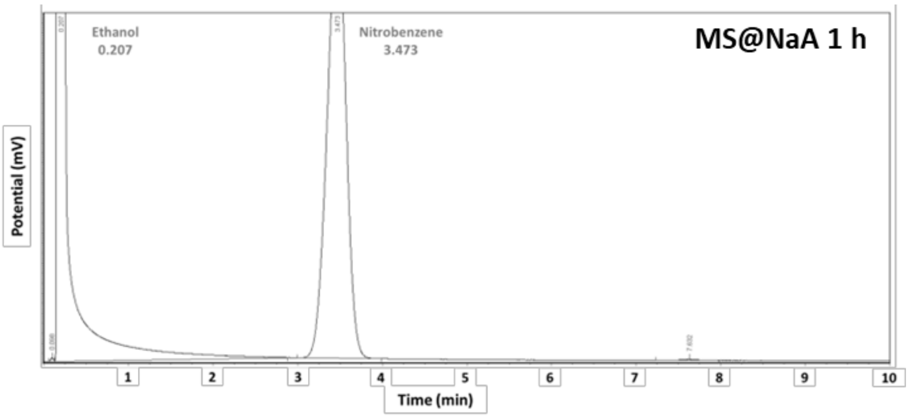

Figure A16 Gas chromatogram of methyl salicylate adsorbs on zeolite NaA for 1 h.

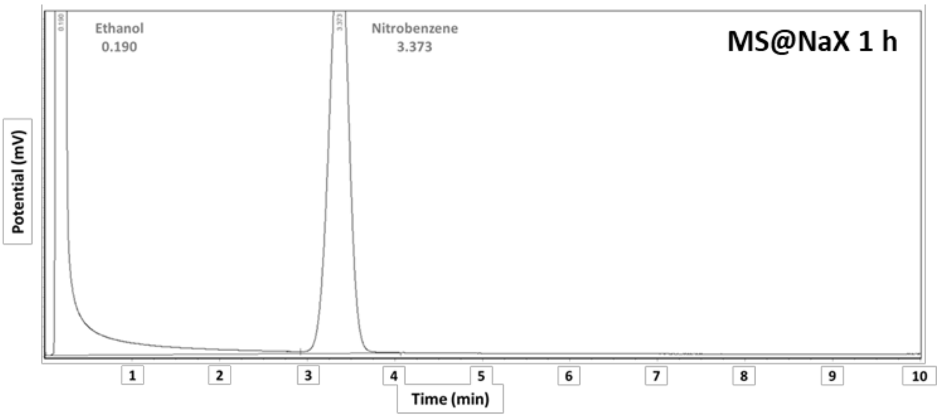

Figure A17 Gas chromatogram of methyl salicylate adsorbs on zeolite NaX for 1 h.

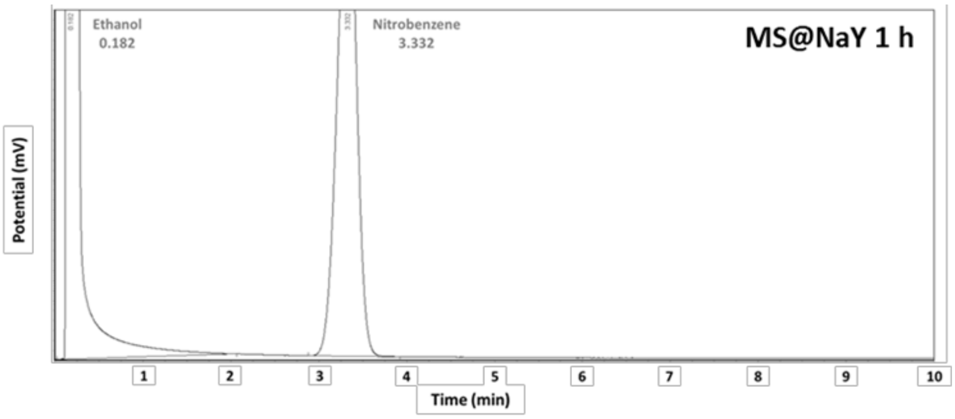

Figure A18 Gas chromatogram of methyl salicylate adsorbs on micron-sized zeolite NaY for 1 h.

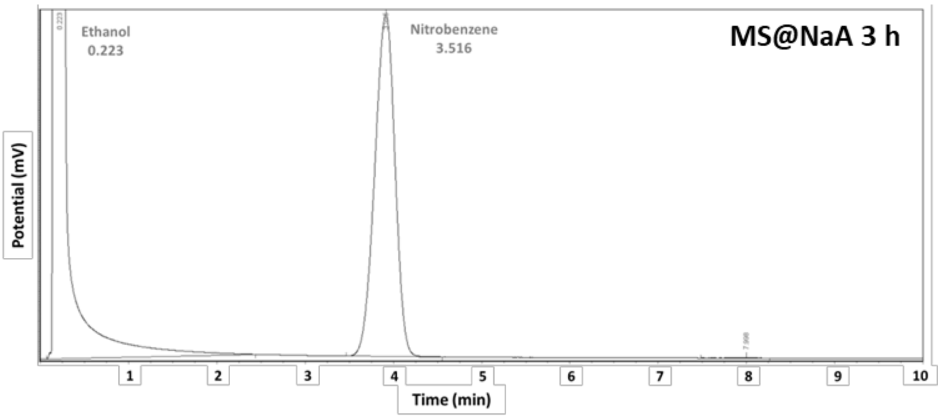

Figure A19 Gas chromatogram of methyl salicylate adsorbs on zeolite NaA for 3 h.

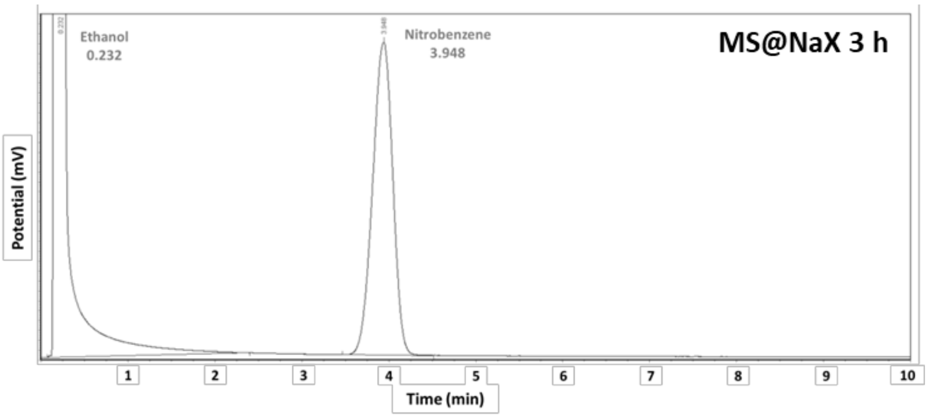

Figure A20 Gas chromatogram of methyl salicylate adsorbs on zeolite NaX for 3 h.

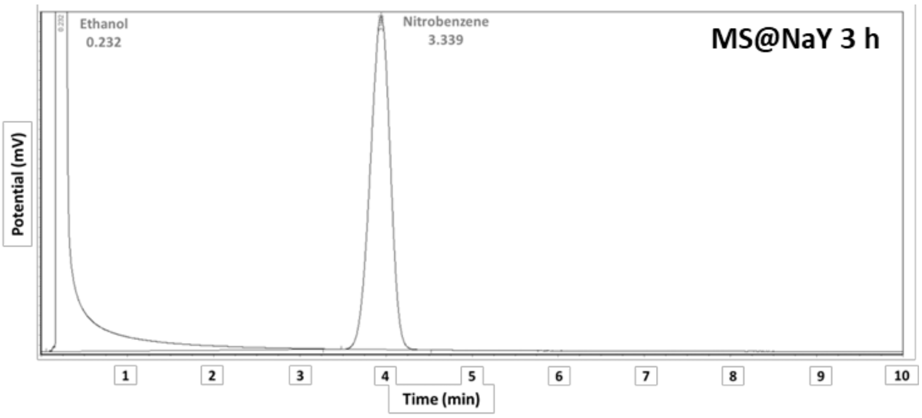

Figure A21 Gas chromatogram of methyl salicylate adsorbs on micron-sized zeolite NaY for 3 h.

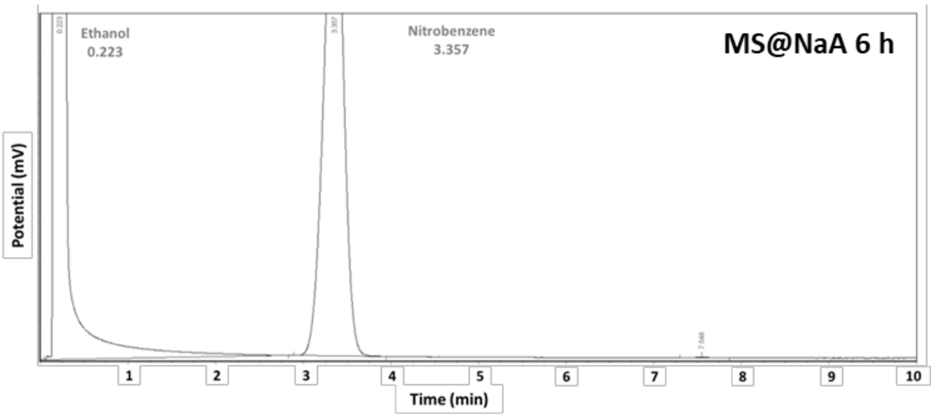

Figure A22 Gas chromatogram of methyl salicylate adsorbs on zeolite NaA for 6 h.

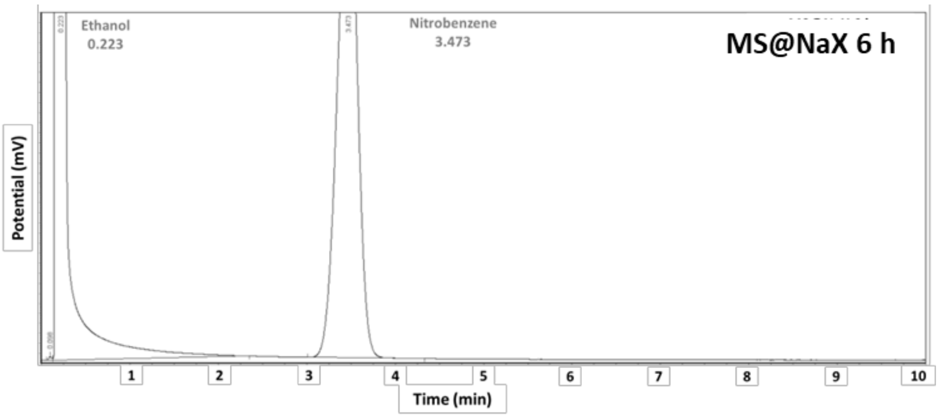

Figure A23 Gas chromatogram of methyl salicylate adsorbs on zeolite NaX for 6 h.

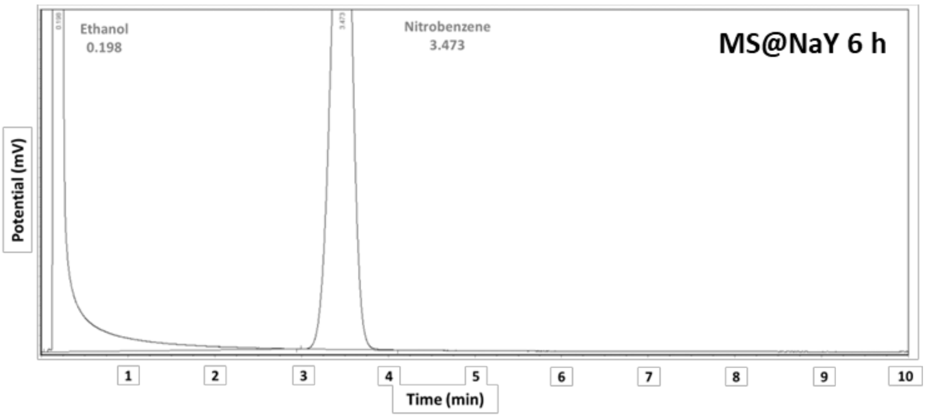

Figure A24 Gas chromatogram of methyl salicylate adsorbs on micron-sized zeolite NaY for 6 h.