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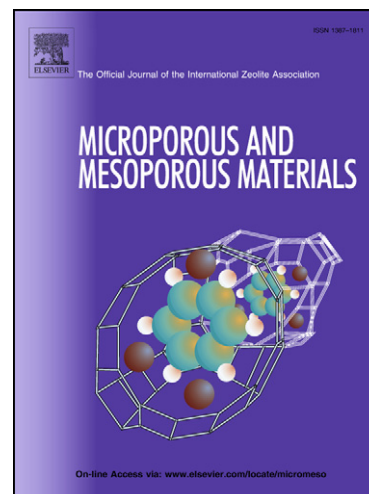
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The effect of pore structure of zeolite on the adsorption of VOCs and their desorption properties by microwave heating

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Abstract

Mordenite and X- or Y-type faujasite were used to remove volatile organic compounds (VOCs) by adsorption at 25 °C. A microwave heating desorption system was applied for pollutant adsorbent regeneration. Studies were focused on the relationship between the adsorption and/or desorption behavior of selected VOCs (benzene, toluene, *o*-, *m*-, *p*-xylene, methanol, ethanol, *iso*-propanol, and methylethylketone: MEK) and the physicochemical properties of the zeolites (i.e. acidity, Si/Al ratio, crystal structure, pore structure, surface area, and pore volume) in this work. It was shown that the adsorption behavior of mordenite zeolites with low surface area depended on its crystal structure, while the faujasite zeolites with large surface area depended on the mesopore volume. Faujasite zeolites showed the greatest adsorption capacity for the selected VOCs. It was also shown that the mesopore volume with ink-bottle pores was advantageous for adsorption and, contrarily, the mesopore volume with cylindrical mesopores was advantageous for VOC desorption and zeolite regeneration. High efficiency desorption of VOCs was obtained using microwave heating. The highest microwave heating desorption efficiency was obtained with molecular sieve 13X due to the cylindrical pore structure.

Keywords: Volatile Organic Compounds (VOCs); Zeolite; Adsorption; Desorption; Microwave heating.

1. Introduction

Volatile organic compounds (VOCs) are present in many types of waste gases, and are

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easily and effectively removed by adsorption process [1,2]. Zeolites and activated carbons are the most common materials used for adsorption of VOCs and are an effective means for collecting these harmful compounds [3,4]. There is therefore a need for research on efficient and economically feasible techniques that actually destroy or recover the pollutants after adsorption. At the same time, the adsorbents have to maintain the effective physical and chemical properties for effective reuse.

Several techniques for adsorbent regeneration have been investigated, including pressure swing, temperature swing, purge gas stripping, displacement, and microwave heating [5]. Regeneration by microwave heating can attain the desired temperature uniformly in a relatively short period (rapid heating), resulting in a lower consumption of energy [6-8]. In addition, regeneration of the adsorbent using microwave irradiation is very effective because the microwave irradiates the VOC molecule directly. Activated carbon could not be used in this study as the adsorbent because it is sensitive to the electric current flow and spark discharge occurs [9]. For this reason, zeolites are the main focus of this work.

In a previous study [10], the relationships between the adsorption capacity and physical properties were investigated for toluene and MEK on various zeolites, followed by an examination of the corresponding zeolite regeneration by microwave heating. It was shown that faujasite showed the greatest adsorption capacity due to the high value of specific surface area and pore volume. Among the physical properties of zeolite, most of the previous experimental studies dealt with N₂ gas physisorption data (specific surface area and pore volume) and the adsorbed amount of toluene and MEK. However, zeolites possess many unique properties such as high adsorption capacity, molecular-sieving effect, thermal stability, and strong acid sites. In addition, the adsorption property of zeolites relates deeply to Si/Al ratios, cation types, pore structures, and acidities [11-13]. Therefore, the effects of these other important parameters were also needed to gain information on the relationships between physicochemical properties and the adsorption behaviors of VOCs on zeolites.

The microwave heating desorption system on zeolites has been widely studied [14-19]. Turner et al. [14] used microwave energy for competitive adsorption of cyclohexane and methanol on silicate. It was shown that microwave heating is more than three times as efficient as conventional heating methods. Alonso et al. [15], also studied the effect of microwave irradiation on the adsorption selectivity and desorption efficiency of VOCs and/or their mixtures from NaY zeolite. Their results show that the microwave irradiation affects the adsorption and desorption on polar molecules more than non-polar molecules. Recently, the desorption kinetics and desorption efficiencies by microwave swing regeneration and

temperature swing regeneration for VOCs on 13X molecular sieve were compared experimentally by Cherbanski et al [18].

Most of the above researchers have focused on the desorption efficiencies of VOCs. Only Polaert et al [17] have reported on the relationship between the dielectric properties of VOCs and micro/meso pore volume of the (NaX) zeolites used in conjunction with microwave heating. It was shown that the pore volume of zeolite is less important than the dielectric properties of the VOCs for desorption efficiency. However, desorption behavior on the zeolite relates to not only pore structure but also adsorption intensity.

In this work, we present a detailed study concerning the evaluation of the effect of physicochemical properties of zeolites on adsorption behaviors. Furthermore, the effect of zeolite pore structure on VOC desorption behaviors by microwave heating for regeneration of zeolites from polluted zeolite was also investigated in more detail.

2. Experimental

2.1. Materials and Characterization

Various commercially available zeolites were used as adsorbents (see Table 1). The as purchased zeolites were manually crushed and sieved to particles in the range of 125 - 140 μm . The water content of the zeolite was measured by treating them in an electric furnace at 300 $^{\circ}\text{C}$ for 24 h in air atmosphere, and were determined from the weight loss after thermal treating.

X-ray diffraction (XRD) patterns for zeolites were identified on a Philips XPERT-PRO X-ray diffractometer operating at 40 kV and a current of 30 mA with $\text{Cu-K}\alpha_1$ radiation (0.154 nm) in the 2θ scan range from 5° to 50° with a step size of 0.04° (Fig. 1). According to the JCPDS powder diffraction database file, it can be seen that the XRD pattern of each zeolites, is in good agreement with the results reported in the literature [20]. This result indicates that the zeolites used in this work possess the highly pure and well-known crystalline structure.

Temperature programmed desorption of ammonia (NH_3 -TPD) to measure the number of acid sites was performed by Lopez-Fonseca et al. [21]. The number of acid sites was obtained by integration of the NH_3 -TPD curves and the results are shown in Table 1.

N_2 adsorption/desorption isotherms were measured at -196°C with a ASAP 2010 analyzer (Micromeritics, USA). The zeolites were outgassed in vacuum at 300 $^{\circ}\text{C}$ for 1 h prior to analysis. Table 1 shows BET specific surface area and pore volume by t -plot. The maximum BET specific surface area was observed on faujasites to be in the range from 540 m^2/g to 604 m^2/g . Total pore volume and mesopore volume on HY901 showed a maximum value of

0.448 cm³/g and 0.260 cm³/g, respectively.

2.2. Adsorption and desorption of VOCs vapor

The experimental apparatus for performing the adsorption and desorption of VOCs vapor was a continuous flow system under atmospheric pressure. Aromatics; benzene (3.58 mol%), toluene (5.90 mol%) and *o*-xylene (0.97 mol%), *m*-xylene (0.95 mol%), *p*-xylene (1.80 mol%), alcohols; methanol (2.88 mol%), ethanol (4.42 mol%), *iso*-propanol (9.94 mol%), and ketone; methylethylketone (MEK, 4.99 mol%) were used as a model gas. All reagents for model gas were GR grade (Junsei Chem.). The concentration of VOC vapor was controlled by vaporizing each VOC vapor in a saturator with helium flow. The Total flow rate of the helium stream containing VOC vapor was kept maintained at 40 mL/min, which was controlled with a mass flow controller (3660, Kofloc). The adsorbent column (i.d.: 7 mm, quartz) of a U-type with a smaller dissipation constant was used. All fittings for fixing the adsorbent column in the oven were made of Teflon unions. Quartz wool was packed to fix the adsorbent bed in the proper location. Variation of VOC vapor concentration during the adsorption experiments was monitored with a gas chromatograph (GC-14B, Shimadzu, Japan) equipped with a thermal conductivity detector (TCD), from which the amounts of VOC vapor adsorbed was obtained.

In the desorption experiments conducted by conventional heating using an electric furnace, the temperature was raised from 25 °C to 300 °C (or 500 °C) at a heating rate of 5 °C/min with a temperature programmer (NP200, Hanyoung, Korea). A commercial microwave heating system, produced by Korea microwave instrument, with an adjustable output power was used (2.45 GHz, 1.5 KW, Korea). The temperature profile of the adsorbent bed during microwave heating was obtained with a sheltered K-type thermocouple, which was inserted into the adsorption bed.

Before adsorption experiments, the adsorbent was pretreated with helium at 300 °C for 1 h with an electric furnace (these conditions can remove up to 98% of the water in zeolites) 0.1 g of the adsorbent was used for each experiment. When the concentration of VOCs in a stream was stable, adsorption was started by passing the stream over the adsorbent bed. After adsorbent bed saturation, the stream containing VOC vapor was changed to pure helium flow by using a six-way valve. Then, reversibly adsorbed VOC vapor was sufficiently desorbed and purged with helium at 25 °C for 1 h before beginning the desorption experiments. Desorption experiments were started once the TCD signal was stable. The components in the effluent gas desorbed by microwave heating were partly analyzed using on-line GC equipped with Porapak Q column (1/8", 6 ft, Stainless steel).

3. Results and Discussion

3.1. Characterization

N_2 gas adsorption/desorption isotherms for all of the used zeolites are shown in Fig. 2. According to the Brunauer-Deming-Deming-Teller (BDDT) classification [22,23], Type 1 isotherms are characteristic of adsorbents containing mainly micropores, while type IV isotherms typically have a hysteresis loop associated with capillary condensation in mesopores. The isotherms of all the used zeolites resembled type IV closely or faintly, suggesting the coexistence of mesopores and micropores [24].

A vertical hysteresis loop of MS13X in the narrow range of $P/P_0 = 0.80$ to 0.99 indicates the presence of limited mesopore volumes in MS13X, and suggests the presence of cylindrical type pores [25,26]. The isotherm for HY901 showed a clear and wide hysteresis loop at relative pressures of ca. 0.45, which is typical for mesoporous zeolite of ink-bottle type pores with pore necks smaller than 4 nm [27]. HY901 had a high proportion of mesoporous volume, which was in good agreement with the result that the mesopore volume of HY901 are about 58 % of total pore volumes in Table 1.

3.2. Adsorption performance

The breakthrough curves for adsorption of various VOCs on the zeolites selected are shown in Fig. 3. For a given concentration, the longer breakthrough time and/or saturation time means a greater adsorption capacity. The breakthrough curves reached adsorption equilibrium, however the breakthrough times were greatly different: HY901 and MS13X required especially longer breakthrough time ($C/C_0 = 0.1$, C_0 and C are initial concentration and outlet concentration, respectively) and/or saturation time ($C/C_0 = 1.0$) when compared to other zeolites. The other zeolites, Z-HM10(2), TSZ-640NAA, Z-HY5.6(2), and Z-HY4.8, have narrow pore necks which may lead to lower adsorption rates, and thus faster breakthrough times.

Fig. 4 shows the amounts of VOCs adsorbed on various zeolites, which were obtained from breakthrough curves in Fig. 3. As a whole, HY901 and MS13X gave the most adsorption capacity for all VOCs. In Table 1, the BET surface area of HY901 and MS13X was similar to that of HY5.6 and HY 4.8, but their adsorption capacities for VOCs was far better. In other words, adsorption capacity for VOCs of the used zeolites did not appear to depend on their BET surface area. HY901 and MS13X consist of higher and lower Si/Al ratio, respectively. Nevertheless, adsorption capacities of HY901 and MS13X were superior to that of mordenites for all VOCs in this work. It was also revealed that Si/Al ratio had no relevant influence on the adsorption properties. HY901 and MS13X had a similar number of acid sites, but they had

relatively fewer of acid sites than the other zeolites studied. From this point of view, acidity of the zeolites seems to be not a main factor in adsorption capacity.

Subsequently, the relationship between the crystal structure and adsorption capacity was investigated. The Adsorption capacity of faujasites was superior to that of mordenites for all VOCs in this work. Crystal structure of zeolite is generally determined by oxygen number. The apertures of faujasite are formed by the 12-member oxygen rings with a free diameter 7.4 Å by 7.4 Å (regular tetrahedron of circularity) providing a maximum free diameter of 13 Å [28]. On the other hand, the apertures of mordenite are formed with the 12-member and 8-member oxygen rings. The straight channels along the x-axis are defined by 12-membered oxygen rings [001] with an elliptical cross section of 6.5 Å by 7.0 Å. These channels are interconnected by sinusoidal channels along the y-axis defined also by complex of 8-member oxygen rings [010] with an elliptical cross section of 2.6 Å by 5.7 Å and 3.7 Å by 4.8 Å, respectively. For this reason, non-aromatic molecules (methanol, ethanol, *iso*-propanol, and MEK) with small kinetic diameters in the range of 3.8 - 5.3 Å can readily adsorb into the mordenites, whereas aromatic molecules (benzene, toluene, *o*-, *m*-, and *p*-xylene) with relatively larger kinetic diameters in the range of 5.8 - 6.8 Å have difficulty being adsorbed due to their larger sizes [29,30]. The amount of VOCs adsorbed on faujasite was greater than that on mordenite because the channel size of faujasite is larger than that of mordenite.

The zeolites in this work had the ink-bottle and/or cylindrical mesopores with average pore size is 10.1 - 10.4 Å sizes of a few nanometers. However, the pores of zeolite in crystal structure are smaller than 7.4 Å. This means that mesopores could not be created in the zeolite structure, indicating that the origin of the mesopores and micropores are naturally different. This suggests the existence of secondary texture properties formed during particles aggregation [31]. We may consider the micropores to be a property of the zeolite structure and reside inside the individual particles, while the mesopores originate from pores created by inter-particle spacing.

Finally, the volume of the pores needed to be considered. Micropore volumes were not correlated to the amounts of VOCs adsorbed even though the size of the micropores and their entrances in crystal structure was larger than the molecular size of adsorbing VOCs. In addition, it was observed that the total pore volume including micropore volume was also not

connected with the adsorption capacity. With all the zeolites used in this work, the amounts of VOCs adsorbed were quite positively correlated with mesopore volume, such as ink-bottle and cylindrical pores, rather than total pore volume.

In summary, the adsorption capacity of HMOR and NaMOR with low surface area depended on its channel size, and the HY5.6, HY4.8, HY901, and MS13X with relatively large surface area depended on the volume of the mesopores. HY901 revealed the most remarkable hysteresis phenomena among the used zeolites, implying that it possessed many ink-bottle shaped mesopores.

3.3. Desorption by conventional and microwave heating

The zeolites polluted with VOCs are in need of heating for their regeneration. The polluted HY901 and MS13X, with larger adsorption capacity for VOCs, were selected for desorption by microwave heating in this work. Characteristics and efficiency for VOC desorption by microwave heating at 500 W of output power were investigated and compared to those by conventional heating using an electric furnace.

When conventional heating was used, the temperature of the adsorbent bed packed with HY901 or MS13X was raised linearly and slowly because of the limit of heat transfer (convection and conduction). When using microwave heating, the bed temperature quickly increased because the microwave could heat the adsorbed VOC molecules directly and homogeneously by dielectric heating. During microwave irradiation on HY901 and MS13X, the temperature of the adsorbent bed was measured separately under helium only, toluene in helium, and MEK in helium.

The variations of adsorbent bed temperature with microwave irradiation time on HY901 and MS13X at 500 W of output power are shown in Fig. 5. The adsorbent bed temperature of both HY901 and MS13X increased with an increase of irradiation time on all streams, and rapidly reached a constant value after about 5 min. The maximum constant temperature attained varied depended upon the gas stream used. MEK was always higher than that of toluene, and both were higher than helium alone. This can be attributed to the difference of dielectric constant, which is the ratio of the electrical conductivity of a dielectric material to free space, of the gas component flowing over the adsorbents. The dielectric constant at STP of helium, toluene, and MEK are 1.00, 2.57, and 18.51, respectively [32]. The maximum temperature obtained by microwave heating of MS13X in a stream of helium only, toluene in helium, and MEK in helium were 147 °C, 150 °C, and 184 °C, respectively, and much higher than that of HY901, that is, 60 °C for helium only, 78 °C for toluene in helium, and

90 °C for MEK in helium. The Adsorbent bed temperature of MS13X was much higher than HY901, even though the dielectric constants of these zeolites are almost same, in the range of 4 - 5. This could be due to the fact that MS13X contains more water which was not removed in the pretreatment process. Water has a high dielectric constant and could significantly affect the temperatures obtained by microwave heating. For reference, the water content for HY901 and MS13X were 4.9wt.% and 20.4wt.%, respectively.

The desorbed amounts of VOCs are divided into reversible and irreversible amounts; the former corresponding to the amount desorbed by just flowing helium at 25°C, and the latter to the amount desorbed by conventional or microwave heating. Table 2 shows the desorption efficiencies of toluene and MEK on HY901 and MS13X by conventional heating and microwave heating. Initial adsorbed amounts were obtained from Fig. 4, and reversible amounts were obtained by flowing pure helium gas only at 25 °C for 1 h, which assumed steady state, because C/C_0 reached a value below 0.05. Desorption efficiency was defined as the ratio of the amount desorbed by heating to the difference of the amount initially adsorbed and the amount that is reversibly adsorbed. Reversible amounts of toluene and MEK on HY901 were much higher than those on MS13X. From this, it can be inferred that HY901 have more physisorbed amounts for toluene and MEK than MS13X.

In conventional heating of MS13X, desorption behaviors at all tested temperatures showed similar desorption efficiencies for both toluene and MEK. In the case of HY901, the desorption efficiencies for toluene were similar to MS13X, but those for MEK were not. The desorption efficiency of MEK on HY901 at 300 °C was very poor, indicating that the affinity of HY901 for MEK (polar) was much stronger than that of toluene (non-polar).

In microwave heating, the desorbed amounts for MEK and toluene were higher than those obtained by conventional heating. This is due to the direct and homogeneous heating from microwave irradiation of the molecules adsorbed on HY901 and MS13X. Furthermore, the amount of MEK desorbed was higher than that for toluene on both HY901 and MS13X due to the difference of dielectric constant between toluene and MEK. A similar conclusion was reported by Alonso et al. [15], where they claim that microwave irradiation can increase the desorption efficiency of polar molecules by a greater degree than non-polar molecules. It was also confirmed that the desorption efficiency by microwave heating was greatly dependent on elapsed time of microwave irradiation. The desorption efficiency for toluene and MEK on MS13X was beyond 100 %. All zeolites were pretreated in an electric furnace at 300 °C for 1

h before conducting the adsorption experiments, but some water and/or impurities might still exist in the pores or on the surface. Their further desorption, resulting in efficiencies beyond 100 %, might be a result of the increase in overall desorption efficiency obtained by using microwave heating rather than conventional heating methods. In both conventional heating and microwave heating, toluene and MEK on MS13X were better desorbed than those on HY901. The reasons for this disparity are not clear, but it was thought to be due to the difference of pore structure on HY901 and MS13X. MS13X has cylindrical mesopores while HY901 has mesopores that are shaped like ink-bottles with a narrow neck and larger inner volume. However, the possibility of residual water in MS13X after pretreatment could not be ruled out because water can increase the temperature of the adsorbent bed when irradiated by microwaves. As a whole, the desorption of VOCs in microwave heating was very efficient compared to conventional heating, and this becomes even more noticeable when the adsorbate is polar.

Based on the above discussion, the amount of VOCs adsorbed on MS13X was lower compared to HY901 due to differences in mesopore volume. On the other hand, desorption efficiencies of MS13X, with cylindrical mesopores, were much higher than those of HY901, which has ink-bottle shaped mesopores. HY901 with greater mesopore volume with ink-bottle pores was advantageous to adsorption for removal of VOCs, and MS13X with appropriate mesopore volume of cylindrical mesopores was advantageous to desorption for regeneration.

4. Conclusions

Adsorption characteristics of the selected VOCs over various zeolites and desorption efficiencies by microwave heating were investigated. Among the various zeolites used in this study, HY901 showed the greatest adsorption capacity due to its larger mesopore volume. It was also observed that the adsorption properties of zeolites for selected VOCs depended strongly on the pore structure. Microwave heating can be expected to be effective for the desorption of toluene and MEK on both MS13X and HY901. However, MS13X shows greater benefits from microwave heating due to its cylindrical pore structure, which is advantageous for VOC desorption. The microwave heating method seemed to be an effective means for the removal of VOCs adsorbed on zeolites.

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Tables

Table 1. The symbol and physical characteristics of various zeolites used in this study

	Zeolites	Symbol	Si/Al ratio ^a	N _{A-S} ^b (mmol-NH ₃ /g)	S _{BET} ^c (m ² /g)	Pore volume (cm ³ /g)		
						V _{total} ^d	V _{micro} ^e	V _{meso} ^f
Mordenite	Z-HM10(2) (JRC)	HMOR	10.2	1.09	270 (81.4)	0.087	0.067	0.050
	TSZ-640NAA (Tosoh)	NaMOR	19.0	0.68	332 (71.2)	0.162	0.143	0.039
Faujasite (Y)	Z-HY5.6(2) (JRC)	HY5.6	5.6	0.88	650 (72.4)	0.228	0.191	0.047
	Z-HY4.8 (JRC)	HY4.8	4.8	0.78	663 (73.2)	0.284	0.240	0.074
	HY901(Zeolyst)	HY901	80.0	0.41	591 (97.1)	0.298	0.188	0.260
Faujasite (X)	Molecular sieve 13X (Aldrich)	MS13X	<1.5	0.47	582 (70.1)	0.215	0.199	0.086

^aData supplied by JRC (Japanese Reference Catalyst), Tosoh, Zeolyst, and Aldrich, respectively.

^bThe number of acid sites by NH₃-TPD data.

^cBET specific surface area, based on the linear part of the 6 point adsorption data at $P/P_0 = 0.06 - 0.20$ (The number in parentheses means BET constant C).

^dCalculated by the Horvath-Kawazoe method at $P/P_0 = 0.97$.

^eMeasured from t -plot method.

^fCalculated by BJH method with the N₂ desorption.

Table 2. Desorption efficiency by conventional heating and microwave heating for toluene and MEK on MS13X and HY901

Zeolites	VOCs	Initial adsorbed amount (mmol/g)	Reversible amount ^a (mmol/g)	Desorbed amount (mmol/g)				
				Irreversible amount (mmol/g)				
				Conventional heating ^b			Microwave heating ^c	
				300 °C	500 °C(1 st)	500 °C(2 nd) ^d	5 min	10 min
MS13X	Toluene	3.7	0.21 (5.7) ^e	0.64 (18.3)	0.65 (18.6)	0.64 (18.3)	0.42 (12.0)	3.57 (102.3)
	MEK	10.8	0.57 (5.3)	3.21 (31.4)	3.51 (34.3)	3.55 (34.7)	2.40 (23.5)	11.58 (113.2)
HY901	Toluene	11.6	2.55 (22.0)	1.58 (17.5)	1.60 (17.7)	1.72 (19.0)	0.13 (1.4)	1.83 (20.2)
	MEK	10.5	3.96 (37.7)	0.15 (2.3)	0.91 (13.9)	1.06 (16.2)	0.39 (6.0)	3.30 (50.5)

^aDesorbed amount by helium gas flow at 25 °C for 1 h.

^bDesorbed amount by temperature program at a heating rate of 5 °C/min.

^cDesorbed amount by microwave heating at 500 W.

^dAdditional re-adsorption at 25 °C followed by 500 °C (1st) experiment.

^eThe number in parentheses refer to desorption efficiency (%), and was calculated by Desorbed amount / (Initial amount – Reversible amount) X 100.

Figure captions

Fig. 1. XRD patterns of various zeolites.

Fig. 2. N₂ gas adsorption/desorption isotherm of various zeolites at -196 °C.

Fig. 3. Breakthrough curves of selected VOCs on various zeolites at 25 °C (●: HMOR, ■: NaMOR, ▲: HY5.6, ▼: HY4.8, ◆: HY901, ●: MS13X).

Fig. 4. Variation of amount of VOCs adsorbed on various zeolites at 25 °C.

Fig. 5. The temperature rising curves by microwave heating at 500 W on HY901 and MS13X under helium, toluene, and MEK stream.

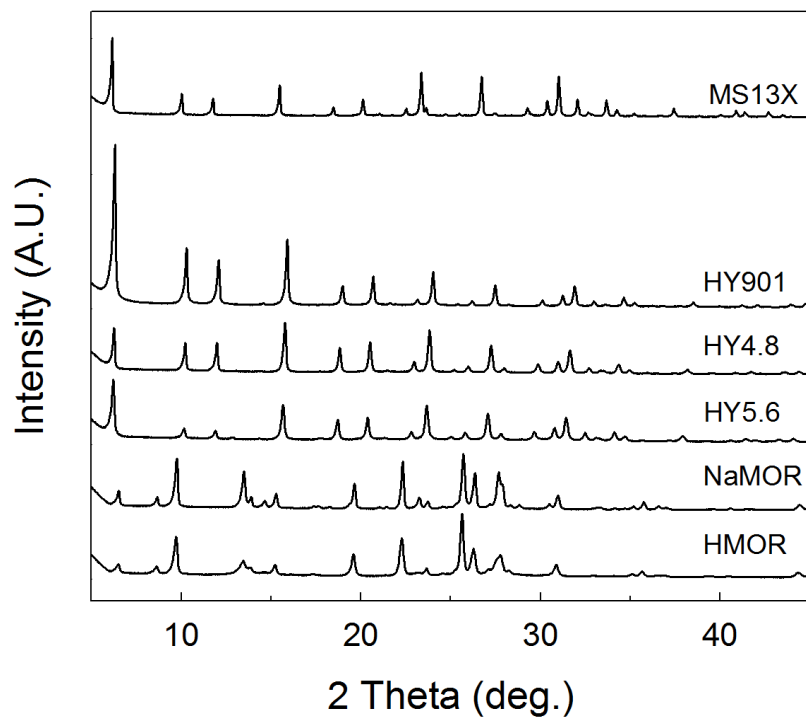


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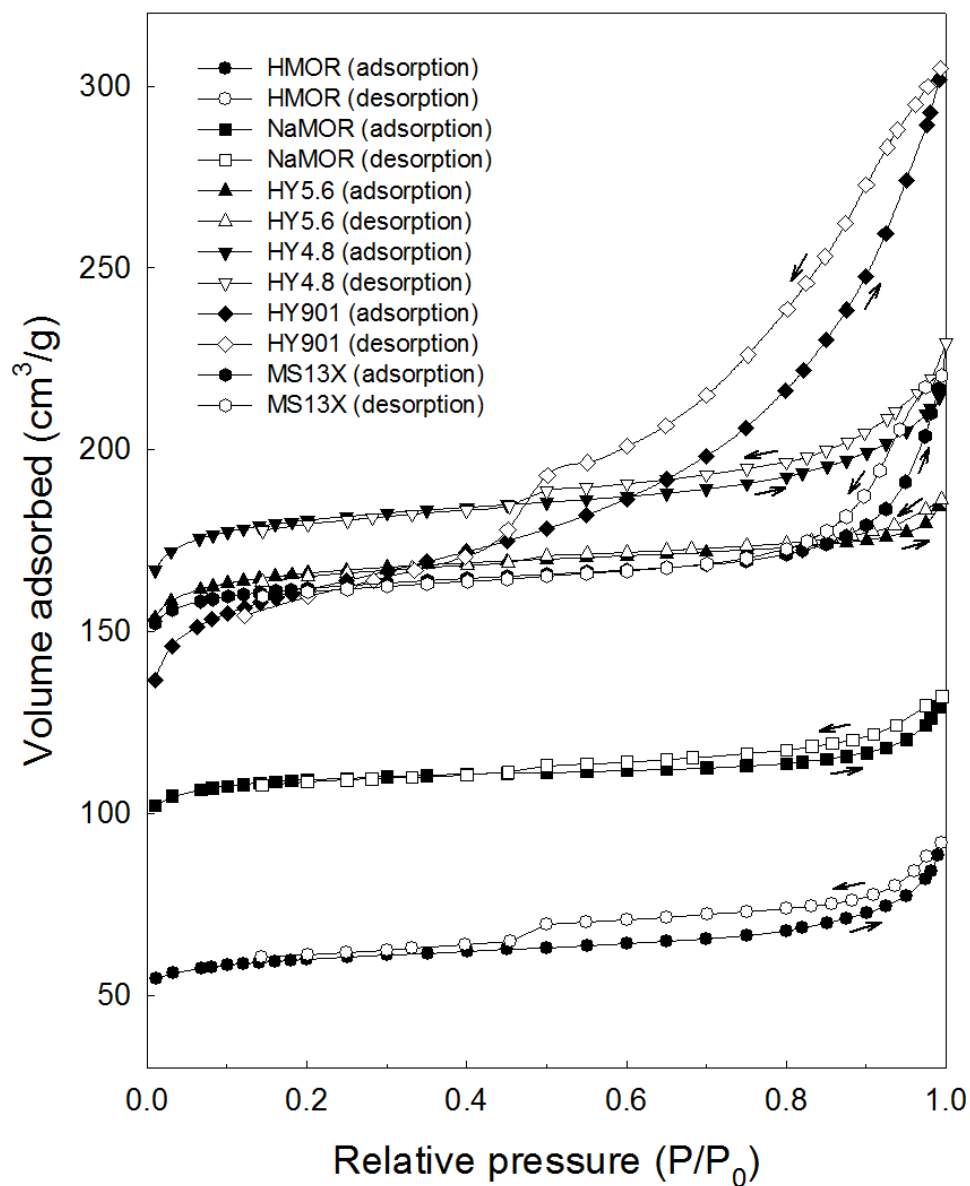


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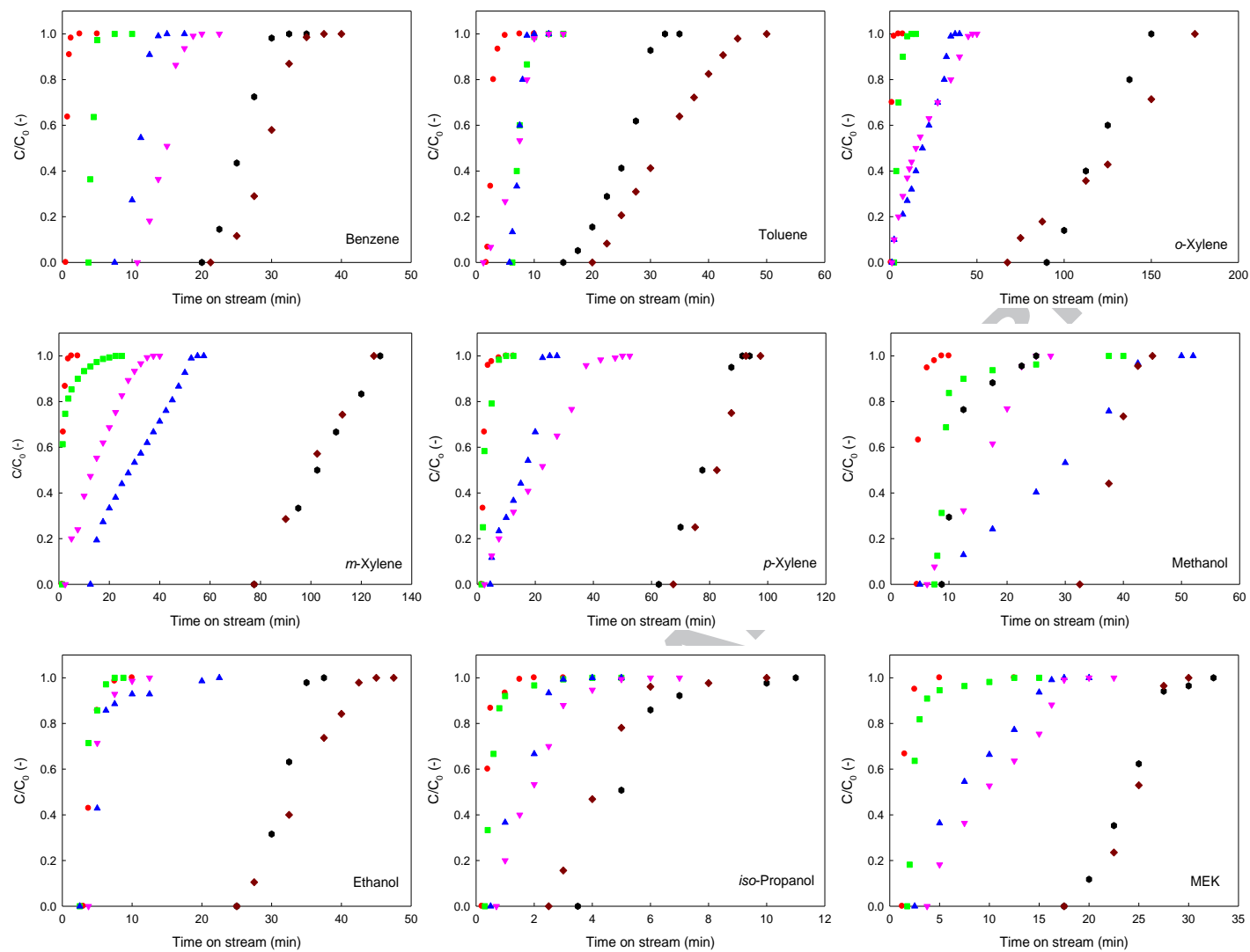


Fig. 3. Breakthrough curves of selected VOCs on various zeolites at 25 °C

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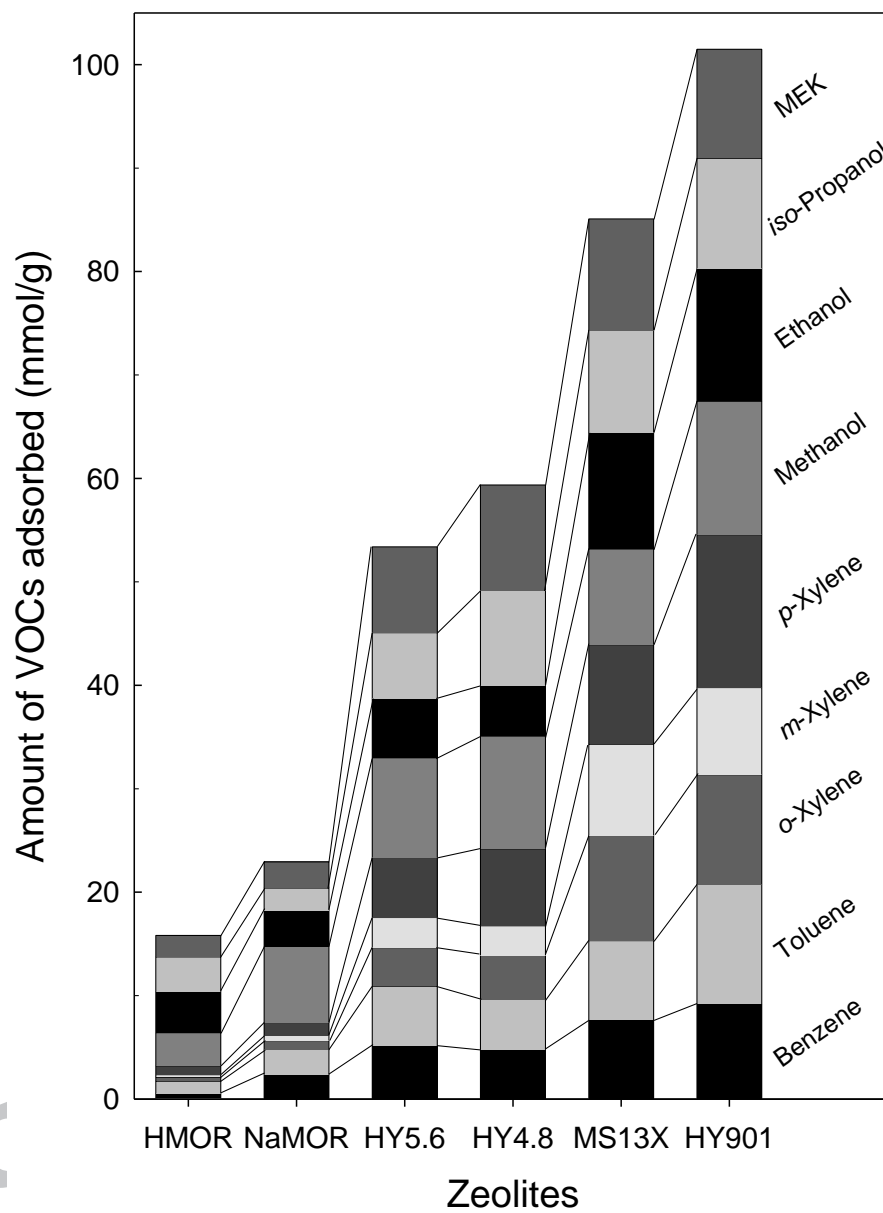


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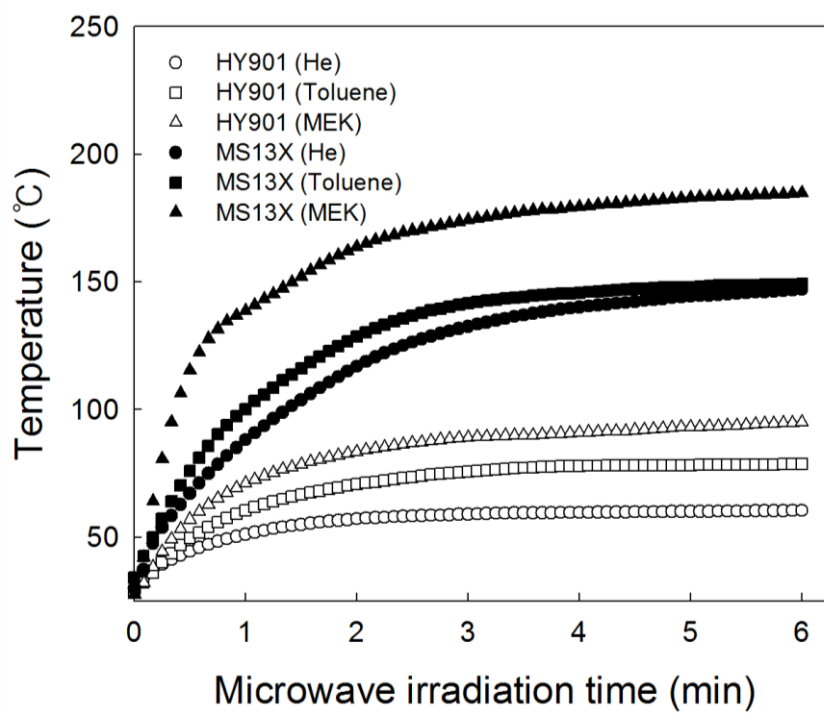


Fig. 5. The temperature rising curves by microwave heating at 500 W on HY901 and MS13X under helium, toluene, and MEK stream.

- Relationship between the adsorption/desorption behavior of selected VOCs and the physicochemical properties of the zeolites were studied.
- Texture in mesopore volumes of zeolite is one of the most influential properties on adsorption capacity of VOCs.
- Mesopore volume with cylindrical mesopore structure lead to the highest desorption efficiency in a microwave heating system.

