Вестник Томского государственного университета. Химия. 2020. № 18. С. 6–17

УДК 661183.6-022.53-026.564.3+665.738.081.3:543.3
DOI: 10.17223/24135542/18/1

O. Zaitceva[1], R. Bingre[2], A.V. Vasilyev[3], B. Louis[2]

[1] Tomsk State University, Institute of Smart Materials and Technologies (Tomsk, Russia)
[2] Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé, Energy and Fuels for a Sustainable Environment Team, Université de Strasbourg (Strasbourg, France)
[3] Saint Petersburg State University (Saint Petersburg, Russia)

Effect of different micro and micro-mesoporosity in Y zeolites and influence of water on toluene adsorption

VOCs (volatile organic compounds) represent a serious problem in industrial plants, especially in China. Among the VOCs, toluene is a common and toxic agent. Adsorption of released toluene is an interesting and very important aspect to preserve the environment and help companies meeting high environmental standards. Zeolites have a high adsorption capacity and can be used to capture VOCs. FAU (Y) type of zeolite is especially well suited for this purpose, due to the ideal micropore size for toluene adsorption. In this article we propose to find the answer to a question that has not been previously studied: how within one group of zeolites the efficiency of adsorption capacity of toluene changes, if we create a variable mesoporosity?

We tested the adsorption capacity of zeolites in two ways. At first, all samples were tested regarding their total adsorption capacity in anhydrous conditions. After selection of the best samples, additional tests of toluene adsorption capacity under wet conditions were carried out. Thus, hydrophilic abilities were checked or in other words, the ability to continue to capture toluene despite the presence of water vapor. This kind of testing conditions brings the laboratory approach closer to real situation in a factory, where obviously there are no ideal conditions.

According to the results of this work, the best adsorption capacity of toluene shows zeolite with an approximately equal ratio of micro- and mesopores. Mesopores provide a high toluene diffusion within the zeolite crystal, and the micropore size of Y-zeolite is ideal for capture toluene molecules.

Keywords: *VOC, toluene, toluene adsorption capacity, zeolite, mesoporous zeolites, microporous zeolites, mesostructuring of zeolites with biomass.*

1. Introduction

VOCs (volatile organic components) are a common problem in industrial plants [1]. The most common examples are ethyl acetate, acetone, benzene, tetrachloroethylene, toluene, xylene and 1,3-butadiene. These VOC are mainly released in companies producing paints, printed materials, plastics, resins, household chemicals.

It is difficult to fully study the effect of these substances on the human body. However, workers who are constantly in contact with these substances have deteriorated health, increased allergic reactions, breath problems, draining mucous membranes and burning feeling in eyes [2].

At the same time, VOCs contribute to the formation of tropospheric ozone and smog [3, 4].

The adsorption method is recognized as an efficient way to reduce VOCs [5]. The main issues in favor of this method are: low operating cost; no chemical degradation and as a result, the possibility of reusing trapped components.

1.1. The choice justification of materials for study

Zeolites have a high adsorption capacity and can be used to capture VOCs. Research in this direction is growing in popularity. The undoubted positive aspects are the possibility to reuse zeolites, the wide variation of zeolite types, high thermal stability, tailorable hydrophilicity [6–8].

Among the volatile organic compounds toluene is a common and toxic agent. Toluene is an organic solvent mainly extracted from oil, coke gas, or as a by-product in certain organic reactions (for example, in the manufacture of styrene).

The domain of application is broad. It is used as a solvent for the production of varnishes and paints, in printing houses (for example, gravure printing). To maintain a high rate of printing the paint contains toluene, as a rapidly evaporating solvent. A significant consumption of this product is also noted in the leather industry (at the stages of dyeing and washing).

According to the literature (for example Takeuchi & Hidaka [9]) we know that zeolite Y exhibits good toluene adsorption abilities. The diameter of a 12-membered ring is 0.74 nm and the diameter of the super-cage in Y zeolites surrounded by 10 sodalite cages is 1,2 nm, while the diameter of toluene molecule is 0.65/0.89 nm. The authors consider that the similarity in size enhances the dispersion interaction.

Thus, we can conclude that the adsorption of released toluene is an interesting and very important aspect to preserve the environment and help companies meeting high environmental standards.

1.2. Literature background

In the publication1 Dong-Geun Lee and others [10] studied adsorption and thermal regeneration two representatives of gases acetone and toluene over Y-zeolite which was dealuminated (Si/Al = 20, BET SA = 704 m^2/g, pore diameter 2.17 nm).

The study reported that the adsorption isotherm of toluene showed Type-I in a large temperature range, whereas in acetone changed from Type-II to Type-III when researchers increased the temperature. Because of different adsorption isotherms, observed different breakthrough results. Adsorption of acetone was higher than toluene, toluene curve was steeper. during the desorption process, acetone could be obtained much more easily. authors explain this dependency to different size of organic molecules.

In the publication Wu *at al* [11], the authors studied the effect of porosity for adsorption-desorption of toluene. 4 materials were used in the work: Y-Na, SBA-15, MCM-41, SiO_2. The worst results on the binding of organic compounds showed SiO_2. This was due to the disorder (irregularity, disorganization) in the structure. MCM-41 authors explain a low adsorption capacity with too specific and large channels of the given material. An interesting result was observed during the testing SBA-15. in this material are present mesopores, which are associated with micropores. very good adsorption results, long breakthrough time. The best adsorption showed Y-Na zeolite. ordering in the structure, ideal size of the micropores for adsorption of toluene, a material rich in sodium, the ions of which are a Lewis acid and provide a strong interaction between the organic molecule and the zeolite framework. It should be noted that reverse order is observed for desorption. the stronger the relationship between adsorbate and adsorbent, the heavier the diffusion and the higher the diffusion temperature is required.

The 2014 the group of Anpo [12] studied the ability of Na-Y, H-Y and USY-H zeolites to adsorb benzene. Using FT-IR and UV methods, it was proved that there is an interaction between benzene and hydroxyl, H and Na ions. This interaction is possible due to the close position of the benzene molecule to the inner wall of the zeolite due to the cation-p interaction between the H and Na ions and between benzene. As a result of this interaction, a vibrational model strongly influences the H.-C. However, the interaction of benzene with the hydroxyl group of the siliceous zeolite shows a less pronounced effect (fig. 1).

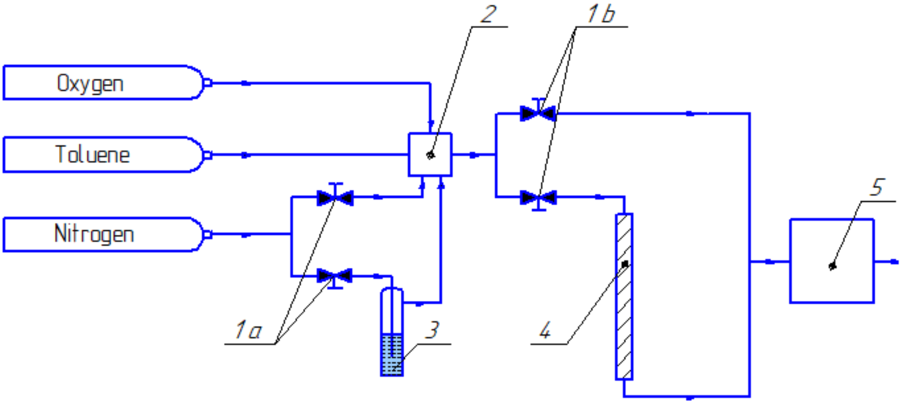


Fig. 1. Schematic image of the setup for the toluene adsorption:
1a, *1b* – stop valve; *2* – mass flow controller; *3* – water saturator; *4* – reactor;
5 – gas chromatograph with a flame ionization detector

In this paper, they also mentioned the experience of previous years regarding the fact that microporous Na-Y, H-Y zeolites are hydrophilic because these zeolites are capable of adsorbing polar water molecules by coordinating the ion-water interaction.

In all the above literature is described in detail: the interaction between the walls of a zeolite and an organic molecule, the influence of an ordered microstructure, a micro-mesoporous structure, an unordered structure for adsorption. It was proved, that microporosity is useful for molecular adsorption, and mesopores are useful for diffusion.

The presence of micro-mesoporosity in the material at the same time may provide a good synergistic effect. But we did not find information about – how within one group of zeolite adsorption efficiency changes, if we create a variable mesoporosity? At the same time, we test our zeolites for the effect of water during adsorption, and ask ourselves a second question – how the different porosity effects on toluene adsorption, if gaseous water is present in the gas mixture, which is very common in manufactures? For these questions we will try to find the answer at the end of this paper.

2. Experimental

2.1. Preparation of the samples

Toluene gas (98 wt. %, Aldrich, USA) was used as adsorptive. Zeolite Y in three surface modifications was used as an adsorbent.

In this paper, commercial microporous zeolite with unchanged sodium ions (Zeochem company, Si/Al = 37) has the code FAU-Na. The same zeolite, but with replaced sodium ions to hydrogen (the Na^+-form was ion-exchanged with an aqueous NH_4NO_3 (1 M) solution, 0.2 g zeolite to 30 ml solution, three times for 1 h at 80 °C and then calcined at 550 °C during 12 h) has the code FAU-H.

Furthermore, commercial micro-mesoporous zeolite (Zeolyst company, CBV-720, Si/Al = 21, H^+-form). This material was given the code CBV-720.

Mesostructuring of zeolites with biomass [13]. Parent zeolite (FAU-Na (0,5g), mixed with the aqueous solution of TEAOH (0.1M, 50 ml) during 10 min, then added to hydrolysis lignin (Saint-Petersburg Forest Technical University) (0,1g) and mixed during 10 min. The whole mixture was quantitatively transferred to an autoclave. After that, it was heated in the oven during 10h at the temperature of 150 °C. Then we cooled down the autoclave to room temperature, filtered, dried for 1 hour at a temperature of 110 °C and calcinated in a muffle oven at 550 °C drying 15 h. This material was given the code A13.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns of zeolites were acquired using a Bruker D8 (Cu Kα) diffractometer operated at 40 kV and 40 mA. XRD patterns were recorded in the $2\theta = 5–60°$ range with a step size of 0.05°. SEM images were acquired in a JEOL FEG-6700F microscope working at a 9 kV accelerating voltage. The textural properties were analyzed by means of nitrogen physisorption using Micromeritics ASAP 2420 equipment. Samples were pre-treated in-situ at 200 °C under vacuum prior to the analyses. Surface areas were determined using the BET method and pore size distributions were obtained using the adsorption branch of the isotherms (BJH method).

2.3. Adsorption of toluene gas

Principle of operation: adsorption of toluene (gas) through Y-zeolite. Registration intensity of toluene signals by GC, break thru time (btt) of each of the studied catalysts, the total adsorption capacity of toluene and influence of water for toluene adsorption

Experimental equipment: the prepared sample (drying at 120 °C overnight) 0.1 g was placed inside the reactor, which is a stainless-steel tube with diameter outside 20 mm, diameter inside 10 mm, 40 cm long. The reactor temperature throughout the experiment was constant and equal 40 °C. The total gas flow is 100ml/min, containing a mixture of three gases toluene, N_2 or Ar, O_2, was controlled by a special mass flow controller performed from the company Beijing Gas Plant «Beiwen». After stabilizing the gas flow to the specified parameters (we worked at 400 ppm), we sent (switched) the gas to the reactor (on the reactor way). To analyze the effluents of the adsorber, we used a gas chromatograph (GC) Agilent Technologies 7890B with a flame ionization detector (or TCD – thermal conductivity detector)

3. Results and discussion

3.1. Textural properties

The following zeolites FAU (Na or H-form), CBV-720 (H-form), A13 (Na or H-form) were selected for testing adsorption capacity of toluene. Fig. 2 shows the results of XRD analysis. Commercial zeolite FAU-Na with the main diffraction peaks at 6.3°, 10.4°, 12.2°, 16°, 19°, 20.7°, 24°, 27.5°, 32° and the high intensity of the signals corresponds to the type Y zeolite.

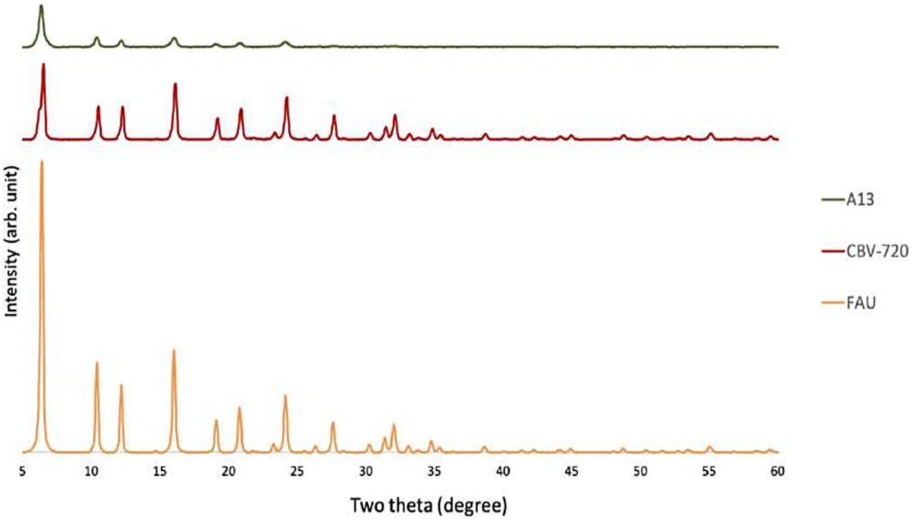
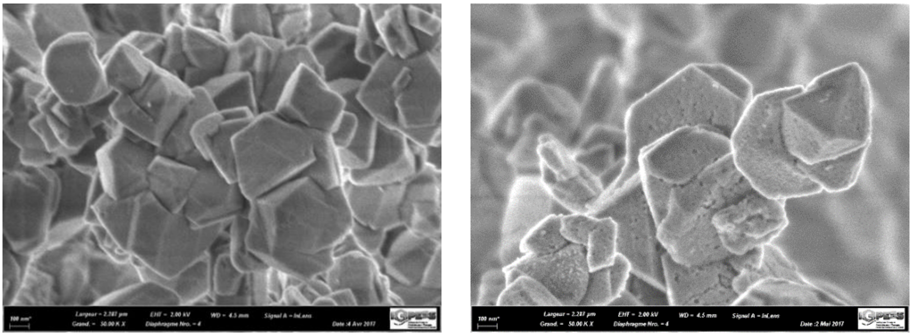
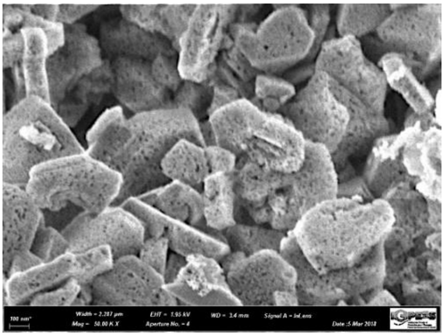


Fig. 2. XRD patterns of the pristine zeolite and mesoporous samples

The peaks of the sample with code CBV-720 remain unchanged. Intensity decreases, this can be explained by small structural destruction due to steaming. A13 retains all of the mentioned above peaks indicate this type of zeolite, but shows the weakest intensity. This can be explained by the prolonged action of the TEAOH on the zeolite and mesostructuring of zeolites with biomass. If we use the ratio: parent zeolite/modified * 100, according to the first, most powerful and characteristic peak, then the percentage of crystallinity retention becomes clear. If for FAU, crystallinity is obviously 100 %, crystallinity dropped to 14 % for CBV, and to 4 % for A4. Additionally, we can be sure that the modified zeolites did not become amorphous due to SEM, the results of which are presented below in fig. 3. Summarizing this study, we can conclude that all 3 types of zeolites have retained a typical structure of type Y or FAU.



FAU CBV-720



A-13

Fig. 3. SEM images of analysed samples

Table 1

BET surface areas, pore volume and pore diameter (max) for microporous and micro-mesoporous zeolites of Y series

Name	Surface Area, m²/g	Micropore Area, m²/g	Pore Volume, cm³/g			Pore diameter, max (nm)
			Total pore volume	Microp. volume	Mesop. volume	
HY	653 ± 15	541	0.31	0.26	0.05	1.2
CBV-720	535 ± 12	452	0.43	0.25	0.18	13
A-13	402 ± 5	146	0.31	0.07	0.24	15

These data are correlated with the BET results in all cases. From FAU to A13 a gradual decrease in micropore area and an increase in mesopore volumes (table 1) can be observed.

Thus, we have zeolites of the same type, but modified in various ways with their own unique textural properties. Having proven zeolites of the same type, but with different porosities, we can proceed to the main topic of our research and start tests our zeolites for adsorption capacity of toluene.

3.2. Toluene adsorption

This work was done at the Beijing Forestry University, in the laboratory EFN led by Professor Qiang Wang. Testing the adsorption capacity of zeolites was performed in two ways. At first, all samples were tested regarding their total adsorption capacity in anhydrous conditions. After selection of the best samples, additional tests of toluene adsorption capacity under wet conditions were carried out. Thus, hydrophilic abilities were checked or in other words, the ability to continue to capture toluene despite the presence of water vapor. This kind of testing conditions brings the laboratory approach closer to real situation in a factory, where obviously there are no ideal conditions. The basic formula for calculating the absorption capacity of toluene formula 1:

$$q = \frac{F \cdot C_0 \cdot 10^{-6}}{W}\left[t_s - \int_0^{t_s} \frac{C_t}{C_0} d_t \right], \qquad (1)$$

where q – absorption capacity of toluene, mg/g; F – gas flow velocity, ml/min; C_t – the concentration of gas at t minutes C_t/C_0, mg/m^3; C_0 – initial concentration of the intake, mg/m^3; W – the amount of zeo, g; t – the absorption time, min; t_s – the time of absorption saturation, min.

All adsorption diagrams can be divided into three segments: a) breakthrough time (btt) that corresponds to the time of complete adsorption of toluene in zeolite; b) stage during which pores of the zeolite can no longer hold all toluene flow and the concentration of the output toluene begins to sharply increase over time (usually, giving a S-shaped curve); c) zeolite channels are filled, the curve of unhurried achievement of the initial concentration ($C/C_0 = 1$) and the end of the activity of the catalyst.

3.2.1. Comparison of the adsorption diagrams FAU (Na/H)

First, the acidic FAU zeolite (FAU-H) and its parent sodium zeolite FAU (FAU-Na) were selected as typical microporous material. The results of toluene adsorption are shown in fig. 4 and 5.

The parent microporous zeolite FAU-Na without any changes exhibits a breakthrough time (btt) value of 43.8 min and absorption capacity of toluene (q) 87.4 mg/g. The same experiment with the acidic version FAU-H, provided very different values: btt 17.5 min and capacity 55.6 mg/g (table 2).

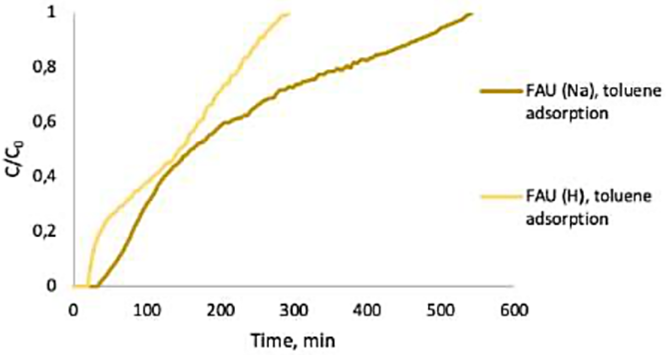


Fig. 4. Toluene adsorption diagrams of FAU (Na/H)

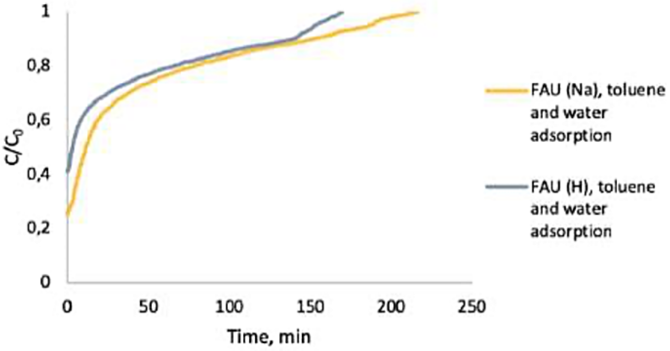


Fig. 5. Toluene adsorption diagrams of FAU (Na/H) in the presence of water

Table 2

Toluene adsorption of FAU (Na/H) in the presence of water or without

Name	Toluene		Toluene + H_2O	
	Breakthrough time (btt), min	Adsorption capacity of toluene (q), mg/g	Breakthrough time, min	Adsorption capacity of toluene (q_{H2O}) mg/g
FAU-Na	43.8	87.4	0	16.63
FAU-H	17.5	55.6	0	12.9

The large differences between breakthrough time and capacity in these experiments can be explained by a stronger chemical interaction between toluene and Na^+ than between toluene and H^+. We made this conclusion on the basis of results published in 2014 by the group of Anpo [12].

Experiments in the presence of water, H- and Na-FAU materials provided very different results (fig. 5). Btt in both cases, decreased to zero, q for FAU-Na decreased from 87.4 to 16.63, and for FAU-H), from 55.6 to 12.9. These results confirmed the information taken from the literature [15] on the high hydrophilicity of microporous zeolites. Microporous Na-Y, H-Y zeolites are hydrophilic because these zeolites are capable of adsorbing polar water molecules by coordination and interaction between zeolites and water.

3.2.2. Comparison of adsorption diagrams with zeolite A-13 (Na/H)

The following tests were performed with zeolite A-13 containing either sodium or proton ions. Zeolites A13 was obtained by mesostructured method in the presence of organic templates. The results of toluene adsorption were surprising (fig. 6).

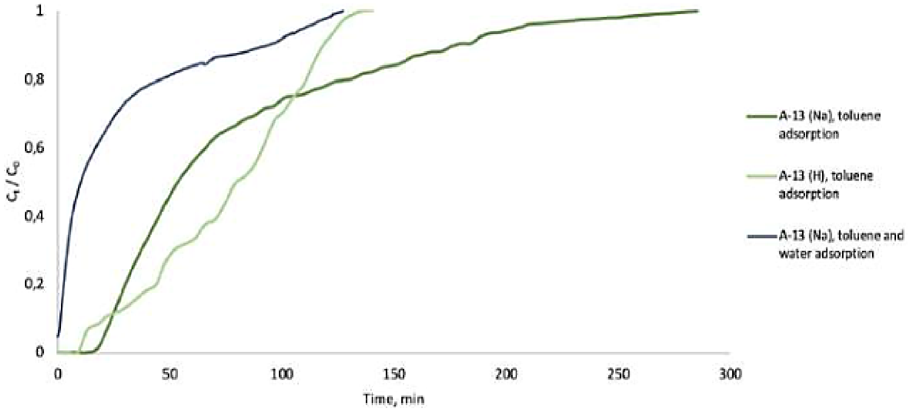


Fig. 6. Toluene adsorption diagrams of A-13 (Na/H) without or in the presence of water

The bbt values are 8.7 for A-13 (H) and 17.5 for A-13 (Na), while the capacities are 30.35 for A-13 (H) and 33.08 for A-13 (Na) (table 3). Although the ratio between the H and Na form remains the same, the adsorption capacity of this zeolite diminished compared to the parent microporous zeolite. This decrease could be due to the fact that the dimensions of the mesopores are large and toluene is simply washed out with the flow of other gases, not having time to adsorb to the surface.

Table 3

Toluene adsorption of A-13 (Na/H) in the presence of water or without

Name	Toluene		Toluene + H_2O	
	Breakthrough time (btt), min	Adsorption capacity of toluene (q), mg/g	Breakthrough time, min	Adsorption capacity of toluene (q_{H2O}) mg/g
A-13 (Na)	17.5	33.08	0.52	10.94
A-13 (H)	8.7	30.35	0	0

A-13 (Na), which showed higher adsorption capacity than the H-form, was also tested in the presence of water. Under such conditions, the bbt value dropped to 0.52 and q = 10.94. These results are also lower than in FAU-Na. But, in percentage, falling adsorption capacity in the experiment for micro-mesoporous zeolite A-13 (Na) was not as low as in the experiment for the microporous zeolite FAU-Na. In sample A-13 (Na) it was 67 %, and in FAU-Na it was 81 %. Adsorption capacity of zeolite A-13 (H) in the presence of water showed 0 adsorption capacity.

3.2.3 Comparison of adsorption diagrams CBV-720 (H)

Commercial zeolite CBV-720, was also evaluated regarding adsorption of toluene and hydrophilicity/hydrophobicity. We used only the proton form of CBV-720. The results are presented in fig. 7.

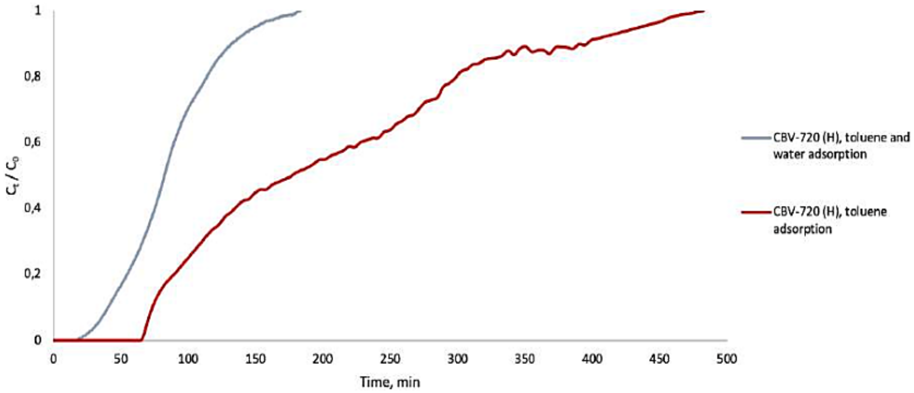


Fig. 7. Toluene adsorption of CBV-720 (H) in the presence of water or without

As can be seen on the adsorption diagram (fig. 7, red curve), the curve (CBV-720 (H), toluene adsorption) has two hills. The first is observed after of 120–200 minutes, the second between 290–370 minutes. It seems logical to assume that these data are correlated to pore size distributions of BET-analysis (fig. 8). The CBV zeolite exhibit clearly two major pore size one well defined from 3 to 6 nm and another set less defined from 7 to 13 nm. Apparently, large volumes of gases penetrate through large mesopores, and then diffused into micropores. In a second stage, the penetration of gases through smaller pores from 3 to 6 nm, sequentially forming the first and second areas on the toluene adsorption diagram.

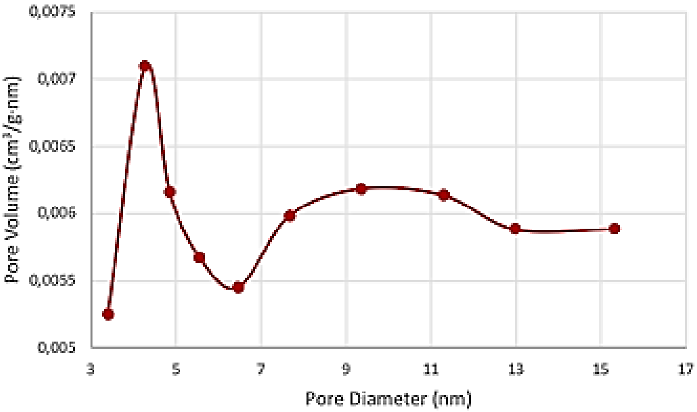


Fig. 8. Pore Size Distribution Of the sample CBV-720

This zeolite exhibits the following values: btt of 65.7 and q = 82.54 (table 4). Its total adsorption is almost the same as the commercial microporous zeolite FAU-Na, that showed the best toluene adsorption. But among the H-forms of zeolites, this adsorption is the highest. This is possible due to the connections between mesopores and micropores.

Table 4

Toluene adsorption of CBV-720 (H) in the presence of water or without

Name	Toluene		Toluene + H_2O	
	Breakthrough time (btt), min	Adsorption capacity of toluene (q), mg/g	Breakthrough time, min	Adsorption capacity of toluene (q_{H2O}) mg/g
CBV-720 (H)	65.7	82.54	31.9	34.89

For this zeolite, water effect on the ability of toluene adsorption was significant. Indeed, btt value fell to 31.9, and the adsorption capacity fell to 34.89 (table 4 and fig. 7, blue curve). These results are the best results from the presented series.

The literature presents some data on the hydrophobicity of dealuminated zeolites. Hydrophobic zeolites are those that are dealuminated and have a minimal amount of hydroxy groups. He tested the CBV-901 CBV-780 CBV-100, in which Si/Al is 41.5, 40, 1.3. According to the results of experiments, CBV-901 was hydrophobic, CBV-780 partially, and CBV-100 hydrophilic. Our study on zeolite CBV-720 (Si/Al = 21), show partial hydrophobicity in agreement with the publication of the Marcus group [16].

4. Conclusion

In this article, we answered the question: how within one group of zeolites (in our case, this is Y-type of zeolites), the adsorption capacity of toluene changes if we test zeolites with variable porosity. In in the row FAU – CBV720 – A13 (H-form), from microporous surface to prevailing mesoporosity, (see Table 1), the adsorption capacity of toluene (q, mg/g) is as follows: 55.6 – 82.54 – 30.35. It is obvious that the presence of micro-mesopores in the structure of the zeolite in approximately equal proportions provides the most effective absorption. The same dependence is observed if we add water vapor to the toluene flow. In the series FAU – CBV720 – A13 (H-form), the adsorption capacity of toluene, (q, mg/g) looks as follows: 12.9 – 34.89 – 0.

Acknowledgements

The authors would like to thank Thierry Romero for SEM images and Aleksander Vasilyev for providing lignin.

References

1. Xie, Z.-Z.; Wang, L.; Cheng, G.; Shi, L.; Zhang, Y.-B. *Journal of the Air & Waste Management Association*. 2016; 66(12); 1224–1236.

2. Disease Control and Prevention (CDC) Organization https://www.cdc.gov/nceh/clusters/fallon/glossary-voc.pdf
3. Lillo-Rodenas, M.A.; Cazorla-Amoros, D.; Linares-Solano, A. *Carbon*. 2005, 43 (8), 1758–1767.
4. Qin, Y.; Wang, Y.; Wang, H.; Gao, J.; Qu, Z. *Procedia Environ. Sci*. 2013, 18, 366–371.
5. Zhang, W.; Qu, Z.; Li, X.; Wang, Y.; Ma, D.; Wu, J. J. *Environ. Sci*. (China). 2012, 24 (3), 520–528.
6. Zaitan, H.; Manero, M.H.; Valdes, H. *Journal of Environmental Sciences* (Beijing, China). 2016, 41, 59–68.
7. Pasti, L.; Rodeghero, E.; Sarti, E.; Bosi, V.; Cavazzini, A.; Bagatin, R.; Martucci, A. *RSC Advances*. 2016, 6(59), 54544–54552.
8. Valdés, H.; Solar, V.A.; Cabrera, E.H.; Veloso, A.F.; Zaror, C.A. *Chemical Engineering Journal*. 2014, 244, 117–127.
9. Takeuchi, M.; Hidaka, M.; Anpo, M. *Res. Chem. Intermed*. 2014, 40 (6), 2315–2325.
10. Lee, D.-G.; Kim, J.-H.; Lee, C.-H. *Separation and Purification Technology*. 2011, 77(3), 312–324.
11. Zhang, W.; Qu, Z.; Li, X.; Wang, Y.; Ma, D.; Wu, J. *Journal of Environmental Sciences* (Beijing, China). 2012, 24(3), 520–528.
12. Takeuchi, M.; Hidaka, M.; Anpo, M. *Research on Chemical Intermediates*. 2014, 40(6), 2315–2325.
13. Zaitceva, O.; Louis, B.; Beneteau, V.; Pale, P.; Shanmugam, S.; Evstigneyev, E. I.; Vasiliev, A.V. *Catalysis Today*. 2020, Ahead of Print.
14. Li, R.; Xue, T.; Bingre, R.; Gao, Y.; Louis, B.; Wang, Q. *ACS Appl. Mater. Interfaces*. 2018, 10 (41), 34834–34839.
15. Sung, C.-Y.; Al Hashimi, S.; McCormick, A.; Cococcioni, M.; Tsapatsis, M. *Microporous and Mesoporous Mater*. 2013, 172, 7–12.
16. Halasz, I.; Kim, S.; Marcus, B. *Molecular Physics*. 2002, 100 (19), 3123–3132.

Information about the authors:
Zaitceva Olesia, Dr. O. Z., Tomsk State University, Institute of Smart Materials and Technologies (Tomsk, Russia). E-mail: zaitcevaolesia@gmail.com
Bingre Rogéria, Dr. R. B., Institut de Chimie et Procédés pour l’Energie, l’Environnement et la Santé, Energy and Fuels for a Sustainable Environment Team, Université de Strasbourg (Strasbourg, France). E-mail: rogeriab.amaral@gmail.com
Vasilyev Aleksander, Prof., Dr. V. A. V. Saint Petersburg State University (Saint Petersburg, Russia). E-mail: aleksvasil@mail.ru
Louis Benoît, Dr. L. B., Institut de Chimie et Procédés pour l’Energie, l’Environnement et la Santé, Energy and Fuels for a Sustainable Environment Team, Université de Strasbourg (Strasbourg, France). E-mail: blouis@unistra.fr