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Competing adsorption of toluene and water on various zeolites

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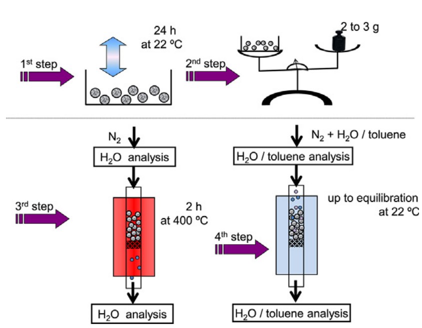
HIGHLIGHTS

- Single and competing adsorption of toluene and water were studied.
- A wide variety of adsorber materials with different hydrophobicities was investigated.
- The sorption behavior varied from almost non-competing to water-driven desorption.
- Strong variations were observed even for the same zeolite type.
- Rules for selection of most appropriate adsorbers were derived.

GRAPHICAL ABSTRACT

Separate and competing adsorption of water and toluene were studied for a wide variety of zeolites.



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ABSTRACT

Decontamination of air or other gas streams loaded with low VOC concentrations is a prevalent task for adsorption using zeolites. Emphasizing the importance of adsorber selection, several zeolites varying in type, Si/Al ratio and provider were tested for toluene as representative organic target compound and water as adsorbate both in single and competing adsorption studies. In some cases, the toluene breakthrough is mainly caused by water-driven desorption. It was shown that for adsorption capacity, kinetics and competition behavior not only type and Si/Al ratio of the zeolite are important but also producer-specific parameters such as crystallinity, binder type and content which are usually not explicitly documented. This study offers a basis for the selection of adsorber materials for treatment of gas streams with significant water contents.

1. Introduction

Volatile organic compounds (VOC) such as organic solvents are prevalent air pollutants originating from many industrial processes but also from stock breeding or remediation of soil and groundwater. In many cases, the sources of contamination are diffuse which results in large contaminated air streams with relatively low and often fluctuating VOC concentrations. Adsorption methods for cleaning of VOC-containing gas streams have been established for many years [1–5]. Depending on the specific process conditions and the relevant hazardous pollutants, the technical realization ranges from simple one-way activated carbon adsorbers to adsorption-wheel technologies adapted for different scales and flow rates. For quasi-continuous operation, combined adsorption/regeneration techniques have been developed [4,6–9]. In the field of air cleaning in the industrial context, the treatment of large air streams with VOC concentrations below 1000 ppmv is an ongoing challenge with broad economic and environmental relevance [10,11]. The large variety of applications can be illustrated by examples from production of various chemicals such as paints [12,13] and from paint finishing systems but also from livestock breeding [14,15], upgrading of natural gas [16–18] or even in air conditioning processes in buildings or cars [2,19–21]. In all these cases,

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Table 1
Overview of investigated materials, providers and selected properties.

Zeolite type	Commercial name or specification	Company	Pellet form and size [mm] [33]	Si/Al ratio	BET_{N2} [m^2/g]
NaX[a]	Köstrolith 13 BFK	CWK[1]	spheres: 1.6 to 2.5	1.17	766
NaX	Zeosorb 13X	Süd-Chemie[2]	spheres: 1.6 to 2.5	< 1.5[b]	702
NaX	SYLOBEAD MS C 544	Grace[3]	spheres: 1.6 to 2.5	< 1.5	708
NaX	13X	Tricat Zeolites[4]	spheres: 2 to 3	< 1.5[b]	379
NaX	Köstrolith NaMSX K2	CWK[1]	spheres: 1.6 to 2.5	< 1.18	732
NaY	LiLSX	Tricat Zeolites[4]	spheres: 1.6 to 2.5	1.5 … 5[b]	870
NaY	SP 562	Grace[3]	spheres: 1.6 to 2.5	5	782
NaY	NaYK	CWK[1]	spheres: 1.6 to 2.5	2.5	695
NaY	Köstrolith UK8	CWK[1]	spheres: 2.5 to 3.5	≥15	490
US-Y	HiSiV 1000	UOP[5]	sticks: Ø = 1.5, l to 3	< 20	423
US-Y	Z700	ZeoChem[6]	spheres: 1 to 2.5	28	517
US-Y	DaY C13	Degussa[7]	sticks: Ø = 3, l to 6	100	608
3A	Zeosorb 3A	Süd-Chemie[2]	spheres: 1.6 to 2.5	1[b]	23
4A	SYLOBEAD® MS 514	Grace[3]	spheres: 1.6 to 2.5	1[b]	23
5A	Köstrolith 5AK	CWK[1]	spheres: 1.6 to 2.5	1[b]	587
5A	Köstrolith 5ABF	CWK[1]	spheres: 1.6 to 2.5	1[b]	651
5A	SYLOBEAD® MS C 522	Grace[3]	spheres: 1.6 to 2.5	1[b]	581
ZSM-5	Z400	ZeoChem[6]	spheres: 1 to 2.5	200	273
ZSM-5	HiSiv3000	UOP[5]	sticks: Ø = 1.5, l to 3	> 20	370
ZSM-5	Köstrolith UZ8	CWK[1]	spheres: 2.5 to 3.5	> 50	316
ZSM-5	FeBEA 25	Süd-Chemie[2]	sticks: 1.6 to 2.5	20 … 25	439
ZSM-5	ZEOcat FM-8	Zeochem[6]	broken pieces < 3.2	15 ± 3	550

[a] Without binder.
[b] Per definition.
[1] CWK Chemiewerk Bad Köstritz, Bad Köstritz, Germany.
[2] Süd-Chemie München (now Clariant), Germany.
[3] Grace GmbH & Co KG, Worms, Germany.
[4] Tricat Zeolites GmbH (now Clariant), Bitterfeld, Germany.
[5] UOP M.S. S.r.I, Reggio Galabria, Italy.
[6] ZeoChem, Uetikom, Switzerland.
[7] Degussa AG (now Evonik Degussa GmbH), Essen, Germany.

specific and optimized clean-up methods are required and, with respect to the technical principle, adsorption techniques are mainly used.

Among the adsorber materials, activated carbons (AC) from various sources are, without any doubt, the most established, well characterized and also relatively cheap materials [22,23]. They are predestinated for the adsorption of hydrophobic organic compounds which closely interact with the large inner surface. Co-adsorption of hydrocarbons can lead to a strong interference when comparing the results with single-component adsorption. Gironi et al. described this competing behavior on the basis of a Langmuir model for methyl *tert*-butyl ether and cyclohexane adsorbed on activated carbon [24]. Based on the individual isotherms the simulation allows predicting the competitive adsorption [25,26]. In contrast, in the present study a hydrophobic hydrocarbon is studied together with water characterized by a multilayer adsorption behavior.

The application of activated carbons is limited for processes were adsorption is combined with thermal regeneration in oxygen-containing gas streams, namely air. Therefore, depending on the type of contamination and the process context, a wide range of non-carbonaceous adsorbents are commercially available and even more are under investigation [27]. Especially, zeolites as a material class with a large variety of the relevant properties (e.g., pore size and shape, hydrophobicity) have been employed for VOC adsorption. Among them, faujasites of type Y are favourable for organic compounds especially for low pollutant concentrations due to their large specific surface area, sorption capacity and shape of the adsorption isotherm [28–30]. Many binder-containing and binder-free zeolite materials are commercially available and partially characterized with respect to the adsorption properties for relevant hydrocarbons. However, the data basis for the practically most relevant application conditions, i.e. for humid gas streams, is limited. This is especially true for ambient air as carrier gas. At ambient temperature (T = 23 °C), a typical relative humidity (rh) of 60% corresponds to a water content of about 12.3 g m^{-3} or 1.66 vol-%. Therefore, a competitive adsorption of the target compounds, hazardous VOC, and water molecules has to be considered in order to evaluate the potential of zeolite materials for off-gas cleaning purposes. Thus, zeolites which are appropriate for VOC adsorption in dry air may be inefficient under real-case conditions in humid air. A key parameter of the zeolites in this context is their surface polarity because the contaminants are usually relatively hydrophobic whereas water strongly interacts with hydrophilic materials. The polarity and therefore the affinity towards hydrophobic and hydrophilic molecules correlates with the Si/Al atomic ratio, alternatively expressed as modulus (SiO_2/Al_2O_3 ratio), of the zeolite framework. Additionally, binder materials can influence the sorption properties of zeolites. While single compound adsorption on zeolites has often been investigated up to now, data on adsorption of gas mixtures containing water are scarce in the literature [31,32].

For applications in adsorption technology and heterogeneous catalysis, a wide variety of zeolites differing in structural type, modulus, type of cation compensating the negative charge of Al in the zeolite framework and binder have been designed. Only a part of them are commercially available. For off-gas cleaning issues, only a handful of zeolites are widely used and in many cases there is a lack of knowledge with respect to competition adsorption properties of these materials.

Therefore, the present study was carried out with 22 different zeolites under well-defined experimental conditions in order to reduce the gap of knowledge in this field. Toluene was chosen as a representative VOC for off-gas cleaning due to its high relevance in practice. The hydrocarbon and water were adsorbed both separately and simultaneously in order to characterize the competitive adsorption. The experiments were made in a packed-bed reactor employing granular zeolite materials.