ADSORPTION OF WATER AND METHANOL ON A NaZSM-5 ZEOLITE
A temperature-programmed desorption (TPD) study

B. Hunger[1]*, S. Matysik[2], M. Heuchel[3] and W.-D. Einicke[2]

[1]Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, D-04103 Leipzig, Germany
[2]Institut für Technische Chemie, Universität Leipzig, D-04103 Leipzig, Germany
[3]GKSS Forschungszentrum Geesthacht, Institut für Chemie, D-14513 Teltow, Germany

Abstract

Using temperature-programmed desorption (TPD), we have investigated the desorption behavior after subsequent co-adsorption of methanol and water and after adsorption of their mixtures on a NaZSM-5 zeolite. The course of desorption indicates that a strong mutual displacement of both components occurs. However, on the strongest adsorption sites methanol is preferentially adsorbed, and already the addition of small amounts of methanol leads to a displacement of water. Our results support the idea of a subdivision of the pore space for adsorption of water/methanol mixtures. Above all, the experiments show that in the part of the pore space where both components are adsorbed, different sites are of importance which vary significantly in their interaction strength.

Keywords: co-adsorption, methanol, mixtures, NaZSM-5, temperature-programmed desorption (TPD), water

Introduction

The thermodynamic treatment of liquid mixture adsorption on zeolites is an important requirement for optimal design of separation processes [1, 2]. However, such investigations of adsorption phenomena allow nearly no information about different adsorption sites, the different adsorbate complexes of the components, and their mutual influence, respectively. But also with regard to application of zeolites as heterogeneous catalysts any knowledge concerning adsorption behavior of reaction mixtures is of great interest (e.g. in methanol conversion on ZSM-5 type zeolites to olefins or gasoline [3, 4]).

Based on previous temperature-programmed desorption (TPD) studies of pure water and methanol on a NaZSM-5 zeolite [5, 6], this contribution is devoted to ob-

---

*   Author for correspondence: Phone: +49 341 9736502, Fax: +49 341 9736399,
      E-mail: hunger@sonne.tachemie.uni-leipzig.de

taining further information about the system by using TPD experiments after preceding co-adsorption or mixture adsorption of water and methanol.

Experimental

The NaZSM-5 zeolite was a commercial material supplied by Chemiewerk Bad Köstritz, Germany. The Si/Al ratio was determined by chemical analysis and by ^{27}Al MAS NMR to be 15. The unit-cell (u.c.) composition of the zeolite is $Na_6[Al_6Si_{90}O_{192}]$. The micropore volume determined by means of nitrogen adsorption at 77 K amount to 0.155 cm^3 g^{-1} [7].

Temperature-programmed desorption was carried out in a flow device with helium as carrier gas (50 cm^3 min^{-1}). For evolved gas detection both a thermal conductivity detector (TCD) and a quadrupole mass spectrometer (Leybold, Transpector CIS System) with a capillary-coupling system were used. For each experiment 100 mg of the hydrated zeolite was used in a mixture with 1 g quartz of the same grain size (0.2…0.4 mm). After activation at 673 K the probes were cooled to room temperature and loaded with water (2.8 mmol g^{-1}) or methanol (2.5 mmol g^{-1}). After this procedure the co-adsorption was performed by adsorption of the second component. Finally, the samples were flushed with helium till no further desorption could be detected. Afterwards the linear temperature program (10 K min^{-1}) was started. During TPD the effluent gas stream was analyzed by means of the mass units for methanol: 31 and 32, water: 18, dimethyl ether: 45 and C3-C5 aliphatic hydrocarbons: 40–44, 56, 58, 70 and 72 amu. Additionally, similar experiments were performed for water/methanol mixtures of different composition ($x_{methanol}$=0.25, 0.50, 0.67 and 0.75). The determination of the desorbed amounts of water and methanol was carried out by an internal calibration of the TCD signal and the 31 and 18 amu responses.

Results and discussion

Figure 1 shows the desorption profiles for water and methanol after adsorption of the corresponding component on the activated NaZSM-5 zeolite. Both desorption curves show a characteristic structure with three distinct ranges. For TPD of methanol in the temperature range between 500 and 650 K the desorption of small amounts of dimethyl ether was observed, indicating a small conversion of methanol. The desorption in the temperature range from 300 up to about 400 K can be assigned to unspecific adsorbed methanol or water respectively [5, 6]. The desorbed amount above 400 K corresponds for both components to the sodium ion content of the zeolite (6 Na^+ per unit cell, or 1.02 mmol g^{-1}). Thus, this desorption range concerns desorption of methanol or water, specifically adsorbed on the sodium ions of the zeolite [5, 6].

Figure 2 shows the desorption curves for water and methanol after adding of 1.1 mmol g^{-1} methanol to a zeolite sample which was before saturated with water under the used experimental conditions. At addition of this small co-adsorbed amount
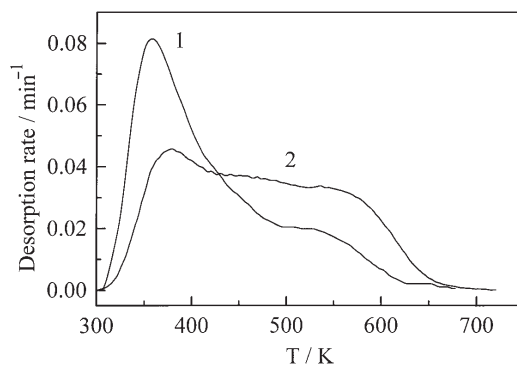
Fig. 1 TPD of water (1) and methanol (2) after adsorption of the pure components on the activated NaZSM-5
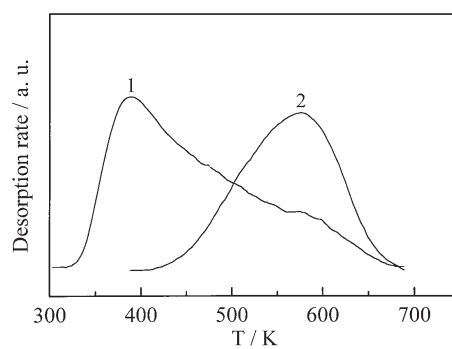

Fig. 2 TPD of water (1) and methanol (2) after co-adsorption of methanol (1.1 mmol g^{-1}) on the water-loaded NaZSM-5
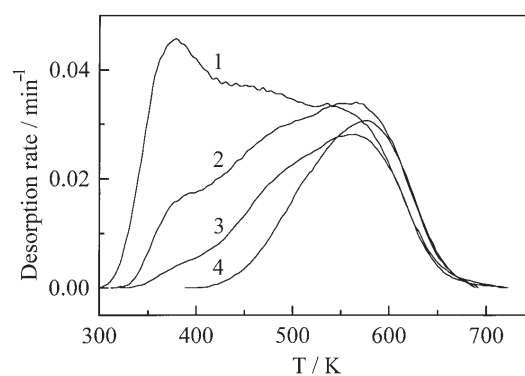

Fig. 3 TPD of methanol after co-adsorption of methanol on the water-loaded NaZSM-5: 1– only methanol adsorption, 2 – 3.4 mmol g^{-1}, 3 – 1.7 mmol g^{-1}, 4 – 1.1 mmol g^{-1}

of methanol, no isothermal desorption of water occurs, i.e., no displacement of water out of the pore system of the zeolite takes place. The methanol is adsorbed additionally. In this case, methanol desorbs at TPD exclusively in the high temperature range above 400 K. In contrast, the addition of larger amounts of methanol results in an isothermal desorption of water and a part of the added methanol does not become adsorbed (Table 1). At the afterwards following non-isothermal desorption, the range at the highest temperatures has always the same intensity as in TPD of the pure component (Fig. 3). Alongside, we see that the enlargement of the added methanol amount increases the desorbed amount in the temperature region of 300–400 and 400–500 K respectively. That is, methanol displaces water out of all three observed adsorbate structures. As apparent from Table 1, about half of the received methanol amount displaces water out of the pore system of the zeolite where the displacement takes place primarily at the strongest adsorption sites. The other half is additionally adsorbed. The non-isothermal desorbed amount of water and methanol adds up in all investigations to about 0.09 ± 0.01 cm^3 g^{-1}, relatively independent on the added amount of methanol and corresponds to a degree of pore filling of about 60% (Table 1).

Table 1 Desorbed amounts of H$_2$O and CH$_3$OH after co-adsorption of methanol or water on NaZSM-5 samples loaded before with the other component (2.8 mmol g^{-1} water or 2.5 mmol g^{-1} methanol)

Co-adsorption/ mmol g^{-1}		Isothermal desorption at 300 K/mmol g^{-1}		Non-isothermal desorption/mmol g^{-1}		Pore filling/ cm^3 g^{-1}
		CH$_3$OH	H$_2$O	CH$_3$OH	H$_2$O	
methanol	1.1	–	–	1.1	2.8	0.095
methanol	1.7	0.5	0.7	1.2	2.1	0.086
methanol	3.4	1.6	0.9	1.8	1.9	0.107
water	1.3	0.5	0.2	1.8	1.1	0.091
water	2.5	1.0	0.2	1.2	2.5	0.094
water	5.1	1.5	2.0	1.0	3.0	0.094
water	7.6	1.8	4.7	0.7	2.8	0.081

At co-adsorption of water on a methanol-loaded NaZSM-5 zeolite sample, always an isothermal desorption of methanol at room temperature was observed (Table 1). That means, water is also able to displace adsorbed methanol out of the zeolite. Since the desorbed amount of methanol in the high temperature range is not decreased (Fig. 4, curve 2), in contrast to co-adsorption of methanol, at addition of small amount of water no replacement of methanol on the strongest adsorption sites seems to occur. Only after addition of larger amounts of water, the intensity is reduced in all desorption ranges. But, also at co-adsorption of water, the total desorbed amount of both water and methanol is always again 0.09 ± 0.01 cm^3 g^{-1} (Table 1).

To derive further information about the mutual impact of the adsorption behavior of water and methanol, we carried out investigations where mixtures of water and methanol were adsorbed on activated NaZSM-5 at room temperature. After addition
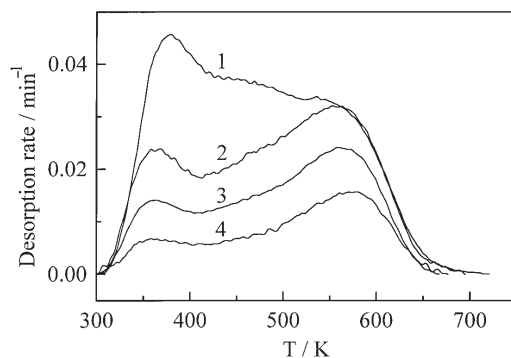
Fig. 4 TPD of methanol after co-adsorption of water on the methanol-loaded NaZSM-5: 1 – without water addition, 2 – 1.3 mmol g^{-1}, 3 – 2.5 mmol g^{-1}, 4 – 7.6 mmol g^{-1}
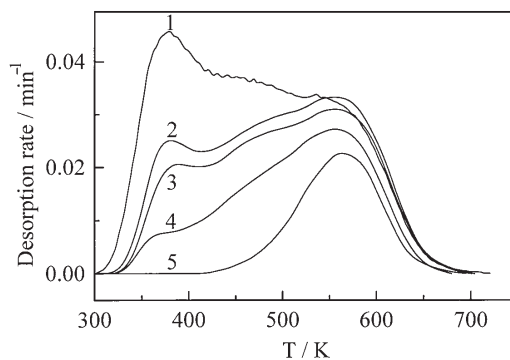

Fig. 5 TPD of methanol after addition of smaller amounts of mixtures at room temperature to the activated NaZSM-5: 1– only methanol adsorption, 2 – $x_{methanol}$=0.75, 3 – $x_{methanol}$=0.67, 4 – $x_{methanol}$=0.50, 5 – $x_{methanol}$=0.25
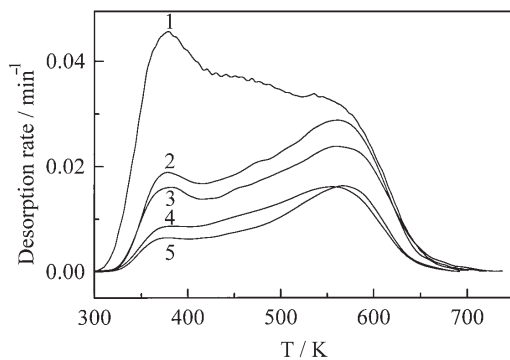

Fig. 6 TPD of methanol after addition of greater amounts of mixtures at room temperature to the activated NaZSM-5: 1 – only methanol adsorption, 2 – $x_{methanol}$=0.75, 3 – $x_{methanol}$=0.67, 4 – $x_{methanol}$=0.50, 5 – $x_{methanol}$=0.25

of mixtures of varying composition in such a total quantity that the total amount was assimilated from the zeolite at room temperature, the desorption behavior of the CH_3OH-TPD (Fig. 5) corresponds to the trend after co-adsorption of methanol on the water-loaded zeolite (Fig. 3). At addition of a mixture with small methanol content, methanol desorbs exclusively in the high temperature range between 500 and 700 K. With increasing methanol proportion in the added mixture, this peak reaches the intensity corresponding to TPD after adsorption with pure methanol. Simultaneously, the intensity of the other two desorption ranges at lower temperatures is increased . If in contrast, the mixtures are added at room temperature in such an amount that a part is not adsorbed at the zeolite, the course of the non-isothermal methanol desorption differs significantly. As can be seen from Fig. 6, it is above all characteristic that, with increasing methanol proportion in the mixture, the intensity of all three desorption ranges of the CH_3OH-TPD is increased relatively uniform. Overall, the course of desorption corresponds to the one after co-adsorption of water (Fig. 4). For a better visualization of the differences during addition of different amounts of mixture, Fig. 7 shows in comparison curves of methanol desorption for mixtures with $x_{methanol}$=0.25. The desorbed amount of methanol is about 2 mmol g^{-1} in both cases (Table 2). After addition of the smaller amounts of mixture, methanol desorbs only at higher temperatures (above about 450 K). In contrast, at addition of larger quantities of the mixture, methanol desorption starts already at 300 K and the desorbed amount is reduced at higher temperatures. This clearly shows the significant changes of adsorption resp. desorption behavior of methanol alone by means of addition of larger amounts of mixture on the activated NaZSM-5.
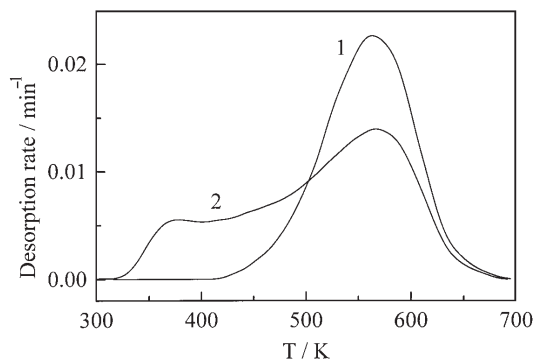

Fig. 7 TPD of methanol after addition of different amounts of the mixtures with $x_{methanol}$=0.25 at room temperature to the activated NaZSM-5: 1 – 2.9 mmol g^{-1}, 2 – 8.9 mmol g^{-1}

As the experiments to co-adsorption of methanol resp. water have already shown, the investigations concerning the adsorption of mixtures also exhibit the fact that a relatively strong mutual influence of the adsorption behavior of both components occurs. This effect cannot alone be explained with the difference in the strength of interaction of the pure components with adsorption sites of the zeolite. The energy

values are for both kinds of interactions, of non-specific interactions and also of specific interactions, for methanol about 10–20 kJ mol^{-1} greater than for water [5, 6], i.e. methanol should always be more strongly adsorbed. But also diffusion effects should not be the reason for the observed behavior. Though the self-diffusion coefficients of water and methanol in mixtures show a dependence on the adsorbed mixture amount, the values are nearly indistinguishable [8]. An explanation for the effects could be the creation of association structures between water and methanol through which the interaction with adsorption sites is weakened, and thus the mutual displacement of water and methanol is relieved. However, at the strongest adsorption sites with an effective desorption energy for methanol of 75–100 kJ mol^{-1}, which is about 14–20 kJ mol^{-1} larger than for water [5, 6], this effect is certainly less pronounced and methanol will be preferentially adsorbed on these sites. This is in accordance with our observation that already the addition of minor quantities of methanol leads to a displacement of water (Fig. 3).

Table 2 Desorbed amounts of H_2O and CH_3OH after adsorption of mixtures

$x_{methanol}$	Added amount of mixture/ mmol g^{-1}	Isothermal desorption at 300 K/mmol g^{-1}		Non-isothermal desorption/mmol g^{-1}		Pore filling/ cm^3 g^{-1}
		CH_3OH	H_2O	CH_3OH	H_2O	
0.25	2.9	–	–	0.6	2.2	0.065
	8.9	1.4	4.7	0.7	2.1	0.065
0.50	2.8	–	–	1.4	1.4	0.082
	8.4	3.3	2.7	0.8	1.5	0.061
0.67	2.9	–	–	1.9	0.8	0.092
	5.6	1.4	1.0	1.3	1.8	0.085
0.75	2.9	–	–	2.1	0.7	0.099
	8.4	4.4	0.8	1.5	1.3	0.083

Our results support the idea of a subdivision of the pore space in adsorption of water/methanol mixtures [2]. Above all, the experiments show that in the part of the pore space, where both components are adsorbed, different sites are of importance which significantly differ in their strength of interaction.

* * *

References

1 W.-D. Einicke, M. Heuchel, M. von Szombathely, P. Bräuer, R. Schöllner and O. Rademacher, J. Chem. Soc., Faraday Trans. I, 85 (1989) 4277.
2 W.-D. Einicke, B. Gläser, R. Lippert and M. Heuchel, J. Chem. Soc., Faraday Trans., 91 (1995) 971.

3 C. D. Chang and A. J. Silvestri, J. Catal., 47 (1977) 249.
4 S. L. Meisel, J. P. McCullogh, C. H. Lechthaler and P. B. Weisz, CHEMTECH, 6 (1976) 86.
5 B. Hunger, M. Heuchel, S. Matysik, K. Beck and W.-D. Einicke, Thermochim. Acta, 269/270 (1995) 599.
6 B. Hunger, S. Matysik, M. Heuchel and W.-D. Einicke, Langmuir, 13 (1997) 6249.
7 B. Gläser, Ph.D. Thesis, University of Leipzig, 1994.
8 J. Caro, M. Bülow, J. Richter-Mendau, J. Kärger, M. Hunger, D. Freude and L. V. C. Rees, J. Chem. Soc., Faraday Trans. I, 83 (1987) 1843.