

THE ADSORPTION OF METHANE ON H-ZSM-5 ZEOLITE

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ABSTRACT

The adsorption of CH₄ on H-ZSM-5 zeolite has been investigated by microbalance technique, ir-spectroscopy and calorimetry. CH₄ is reversibly adsorbed in the temperature range investigated (225 to 723 K). The adsorption can be described by Langmuir isotherms with a heat of adsorption of about 28 kJ/mole. CH₄ shows 3 vibrations in the adsorbed state, the induced ν_1 vibration at 2900 cm⁻¹, the ν_3 vibration at 3005 cm⁻¹ and the induced $2\nu_2$ vibration at 3060 cm⁻¹. The OH-vibration of the Brönsted sites is shifted to lower frequency by the adsorption of CH₄.

INTRODUCTION

The formation of hydrocarbons from methanol on H-ZSM-5 was found around 1970 by the Mobil Oil Corporation (ref. 1). The state of the art is given in a recent review paper by Chang (ref. 2). The products formed are hydrocarbons of carbon numbers C₁ to C₁₀. In this paper we are reporting about the adsorption of CH₄ on H-ZSM-5. The adsorption of CH₄ on NaA, CaA and NaX zeolites (ref. 9) and on vycor silica glass (ref. 11) has been investigated by ir-spectroscopy. CH₄ is molecularly and reversibly adsorbed at low temperatures on these zeolites and the glass. A heat of adsorption of CH₄ on Linde-5A-zeolite of 22.4 kJ/mole has been determined (ref. 10).

EXPERIMENTAL

For the adsorption measurements a vacuum microbalance (Sartorius 4433) of which a schematic diagram is shown in Figure 1 was used. It was attached to an oil diffusion pump to attain an ultimate vacuum of 10⁻⁵ Pa and to a gas manifold for the admission of the various gases. The experiments were performed at temperatures between 77 and 723 K. For the determination of the isotherms the temperature could be kept constant by a cryostat.

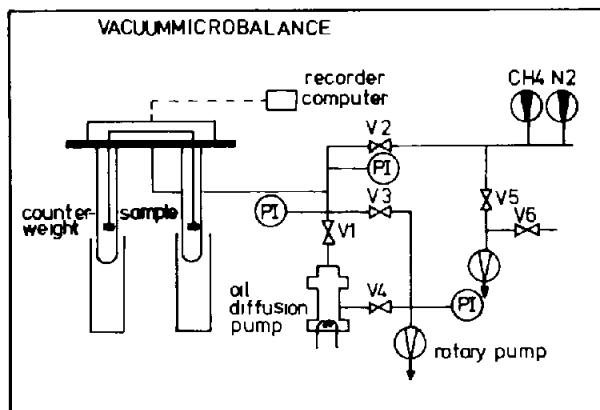


Fig. 1: Schematic of the vacuum microbalance set-up

A detailed description of their set-up has been given previously (ref. 3). Only a short summary will be given here. The spectra were taken with a Perkin-Elmer 580A dual beam spectrometer. The catalyst was pressed in a self-supporting disc and put in one of the two NaCl sealed ir-cells. A continuous gas stream through both cells allowed a compensation of the gasphase surrounding the catalyst.

Calorimetric measurements were performed in a DSC apparatus of Setaram. Two quartz reactors were inserted into the measuring tubes, with Ar flowing through them. In one of them 52.4 mg H-ZSM-5 or, for reference measurements, a similar amount of quartz powder was located on a porous plate in the heat sensitive zone of the calorimeter. The second reactor was used as a thermal reference. The gas flow was measured by capillary flowmeters, the pressure drop over the sample reactor was gauged by a mercury manometer. The flow rates of 3.2 and 7.1 ml/min could be controlled to be within 1%. All experiments have been performed at 30 °C. Two sample loops of 1 and 10 ml were used. With these, pulses of 1% CH₄ in Ar, pure CH₄ and He could be added to the Ar flow. Gas analysis was performed by a gas chromatograph with FID. A two channel chart recorder allowed the simultaneous plotting of the

heat flow signal of the calorimeter and the methane concentration signal of the gas chromatograph. Because of the identical flow pattern, changes of the concentration peak could be directly related to adsorption processes.

To obtain the H-form of the zeolite the Na⁺-ions were exchanged by 0.1 M HCl at room temperature; the degree of exchange was about 70%. The Si/Al ratio was 52 which produced 1.3 acidic Brönsted centers per unit cell of the zeolite or 2.2×10^{-4} mole/g zeolite. The dimensions of the orthorombic unit cell are: $a = 2.03$ nm, $b = 1.98$ nm, $c = 1.35$ nm. The BET surface area was determined by N₂ adsorption at 77 K (t-plot method) and amounted to about 80 m²/g.

RESULTS AND DISCUSSION

Ir-spectroscopy

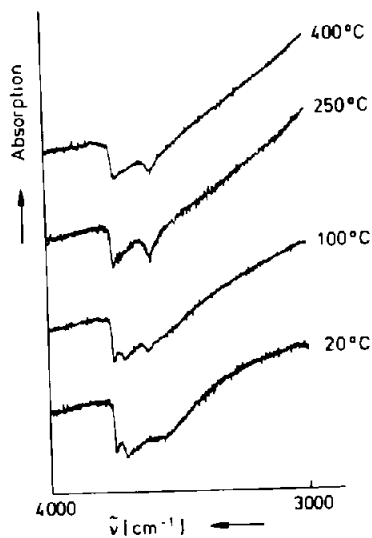


Fig. 2: The influence of calcination of H-ZSM-5 on its OH-vibrations

H-ZSM-5 was calcined at 450 °C in He atmosphere. The change in the OH-vibration region during calcination is shown in Figure 2. Bands at 3740, 3670 and 3560 cm^{-1} due to OH-vibrations are visible at low temperatures. At 100 °C the band at 3560 cm^{-1} vanished and a band at 3605 cm^{-1} appeared. At even higher temperatures only the bands at 3740 and 3605 cm^{-1} remained. After cooling H-ZSM-5 in dry atmosphere to room temperature the ir-spectrum is identical to that at 450 °C. The observed sequence of the change of the OH-vibrations during calcination is in accordance with literature results (ref. 4-6). The OH-vibration band at 3740 cm^{-1} is due to weak acidic terminal silanol groups. The band at 3605 cm^{-1} corresponds to the strong acidic Brønsted group (Si-OH-Al) which is catalytically active. At lower temperature this vibration is obstructed by weakly bound water molecules, which produce the bands at 3670 and 3560 cm^{-1} .

The effect of the adsorption of methane at 288 K on the ir-spectrum of H-ZSM-5 is shown in Figure 3. The lower spectrum de-

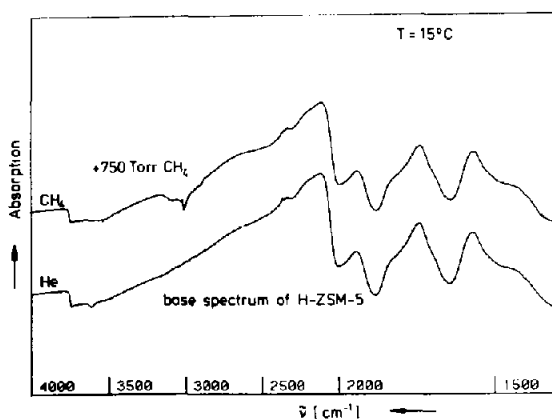


Fig. 3: Ir-spectrum of clean H-ZSM-5 and after adsorption of methane at 750 Torr

picts the clean H-ZSM-5 zeolite. The two OH-vibrations are clearly visible. The bands below 2500 cm^{-1} belong to the Si-O skeleton vibrations. Similar bands have been found in SiO_2 and $\text{SiO}_2/\text{Al}_2\text{O}_3$ mixtures (ref. 7, 8). These vibrations are independent of temperature and CH_4 adsorption. The upper spectrum was taken at a constant methane pressure of 750 Torr. Vibration bands due to CH_4 appear around 3000 cm^{-1} and the Brönsted OH-vibration at 3605 cm^{-1} vanishes. To see the effect of methane adsorption more clearly difference spectra, i.e. the spectrum of H-ZSM-5 with adsorbed CH_4 minus the spectrum of clean H-ZSM-5, were derived. These are drawn in Figure 4 for different temperatures and at a constant methane pressure of 1 bar. The negative peak at 3605 cm^{-1} shows that the

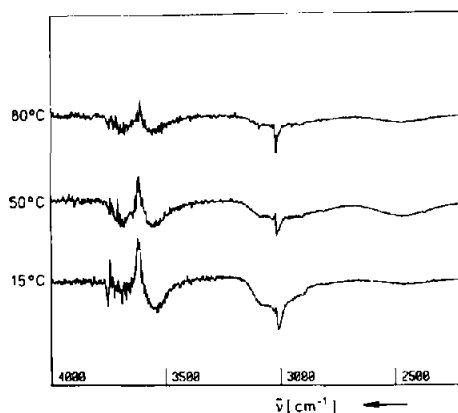


Fig. 4: Difference spectra after methane adsorption on H-ZSM-5 (spectrum of the CH_4 covered H-ZSM-5/spectrum of the clean H-ZSM-5)

OH-vibration disappears with the adsorption of CH_4 . Simultaneously a broad positive peak is observed at 3560 cm^{-1} . Vibrations of methane are visible at 3060 , 3005 and 2900 cm^{-1} . The intensity of the positive and negative maxima is dependent on temperature, which means that the adsorbed amount decreases with increasing

temperature. A comparison of vibrational data of CH₄ in the gas-phase and CH₄ adsorbed on zeolites is given in Table 1.

TABLE 1:

Vibrational Bands of CH₄ [cm⁻¹]

	Gas	H-ZSM-5	NaA ^{+))}	NaX ^{+))}	
v ₄	1306 (IR)	-	1312	1306	
v ₁	2914 (Raman)	2900	2885	2888	
v ₃	3020 (IR)	3005	3000	3004	
2v ₂	3071.5 (Ra.)	3060			+)ref. 9

The v₄-vibration around 1300 cm⁻¹ was not observed in our case, since H-ZSM-5 is not transparent in this region. In agreement with literature results on NaA and NaX zeolites we find an induced v₁- and a v₃-vibration. In addition, an induced 2v₂-vibration exists at 3060 cm⁻¹. The occurrence of the two induced vibrations proves the existence of a strong electric field at the channel intersections. The rotational broadening of the v₃ band shows that the channel system of H-ZSM-5 is wide enough for some remaining rotational freedom. More over the width of the induced v₁-vibration can be explained by translational freedom of CH₄ in the channel system. All the three observed bands are shifted to lower frequencies. The disappearance of the Brönsted OH-vibration at 3605 cm⁻¹ during the adsorption of methane indicates the strong interaction of the acidic group with the adsorbed molecules.

Adsorption measurements

To investigate the type of adsorption, isotherms have been performed with the vacuum microbalance. The adsorption isotherms from which the type of adsorption was derived are given in Figure 5 for temperatures between -17 °C and 67 °C. The adsorbed amount increases with increasing pressure and with decreasing temperature. The reversibility of the isotherms was checked by pumping

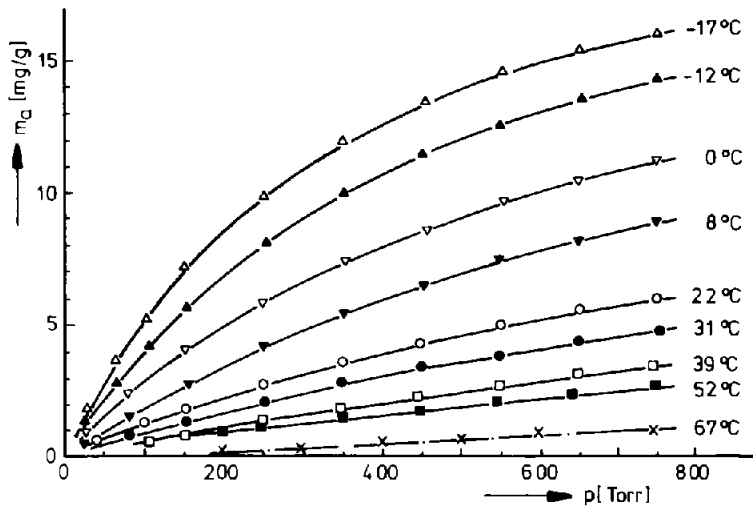


Fig. 5: Adsorption isotherms of CH_4 on H-ZSM-5

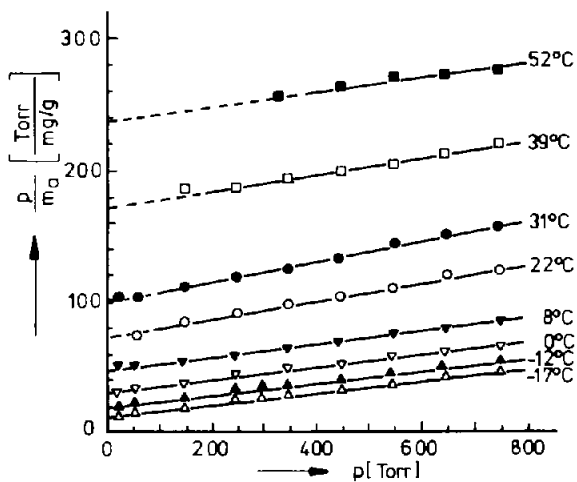


Fig. 6: Linearized Langmuir plots for CH_4 adsorption on H-ZSM-5

off the CH₄. In order to test whether adsorption corresponds to the Langmuir equation the results were plotted according to the linearised Langmuir formula:

$$\frac{p}{m_a} = \frac{1}{m_s b} - \frac{1}{m_s} p$$

in Figure 6 (m_a = adsorbed amount [mg/g_{cat}]; m_s = maximum coverage [mg/g_{cat}]).

One can see from Figure 6 that the above equation is very well fulfilled. This makes the Langmuir type adsorption very likely in this case. m_s amounts to 21 ± 1 mg/g, i.e. $1.3 \cdot 10^{-3}$ mole/g_{cat}. For Langmuir adsorption the heats of adsorption have to be independent of coverage. The isosteric heat of adsorption (q_{st}) can be determined by the Clausius-Clapeyron equation:

$$\left(\frac{d \ln p}{d(1/T)} \right)_{m_a} = - \frac{q_{st}}{R}$$

A necessary supposition for the applicability of this equation is equilibrium between gasphase and adsorbate, which was verified in our case. The isosteres for different coverages are shown in Figure 7. Again, very good straight lines are observed, which are pa-

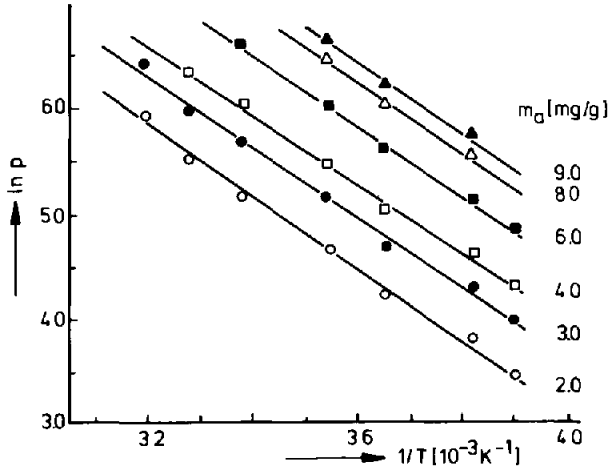


Fig. 7: Isosteres for CH₄ adsorption on H-ZSM-5

parallel to each other. The evaluated heat of adsorption is 28.2 ± 0.5 kJ/mole and is independent of coverage as expected for Langmuir isotherms. Of course, the heat of adsorption can also be determined from the temperature dependence of the Langmuir constant b . An Arrhenius plot shows a straight line, the evaluation of the slope results in a heat of adsorption of 25 ± 3 kJ/mole in accordance with the above value. A comparison with the heat of condensation of methane of 8.2 kJ/mole leads to the assumption that it is weakly chemisorbed on H-ZSM-5. The binding energy is slightly higher than on Linde-5A-zeolite, for which a value of 22.4 kJ/mole has been reported (ref. 10). From the fact that the adsorption of CH_4 on H-ZSM-5 obeys the Langmuir equation we can draw the conclusion that there are no lateral interactions between the adsorbed molecules, despite the fact that about six molecules CH_4 are adsorbed per one acidic Brönsted center.

Calorimetric measurements

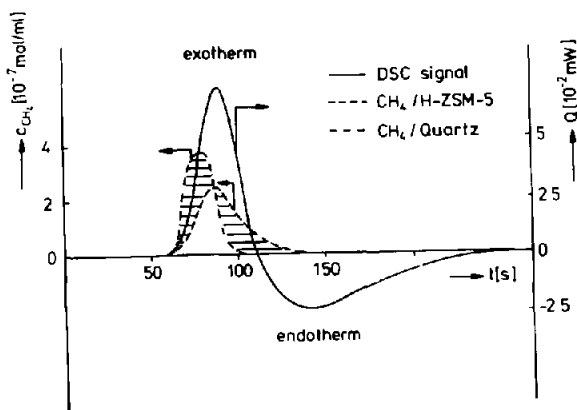


Fig. 8: Concentration and heat signal of a methane pulse (1 ml 1 % CH_4/Ar) over H-ZSM-5 and quartz

Firstly, we report about experiments with 1 ml pulses of 1 % CH₄ in Ar. The thermal effect during adsorption and desorption and the methane concentration at the outlet are shown in Figure 8. With quartz powder used as reference in the reactor no heat effects could be observed; the methane pulse reached the gas detector in almost symmetric form and exhibited in the peak maximum still 95 % of the original concentration in the sample loop. With the CH₄ pulses flowing over H-ZSM-5, the concentration maximum was smaller and arrived later. The differences in the concentration pulses are due to the adsorption on H-ZSM-5 (cf. shaded area on the left side of Figure 8) which is followed by desorption (the gas reaching the detector later in time).

When CH₄ adsorbs on H-ZSM-5, an exothermic heat evolution can be observed, which is followed by an identical endothermic heat pulse after the CH₄ has passed the zeolite. Because of the slow heat conduction from H-ZSM-5 to the heat detector of the calorimeter a partial compensation of the heats of adsorption and desorption occurs. This makes a quantitative evaluation impossible.

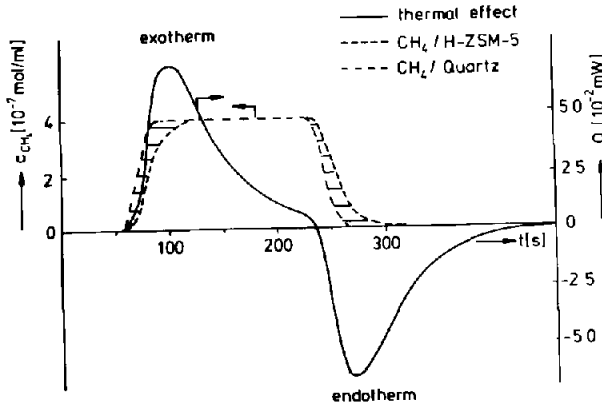


Fig. 9: Concentration and heat signal of a methane pulse (10 ml 1% CH₄/Ar) over H-ZSM-5 and quartz

To separate adsorption and desorption, we used a 10 ml sample loop in the following experiments. The results are presented in Figure 9. The concentrations of methane after flowing over quartz or H-ZSM-5 reached a constant and identical value, which shows that adsorption equilibrium was reached on H-ZSM-5. On the zeolite the constant concentration was approached later than on quartz. The CH₄ pulse is long enough to almost completely separate the heats of adsorption and desorption (cf. Figure 9). The change over of the calorimetric signal into the endothermic region is accompanied by a decrease in the concentration of methane. The equilibrium coverage of CH₄ on H-ZSM-5 evaluated from the missing (shaded) concentration area with a methane partial pressure of 9.9 Torr at 30 °C is 0.089 + 0.008 mg/g, which compares very well with 0.081 mg/g obtained by gravimetric measurements. The heat of adsorption evaluated from the calorimetric signals of Figure 9 amounts to 19.6 kJ/mole. This is well below the values reported before.

The reason for this discrepancy between the heats of adsorption determined by the two methods can be found by experiments with pulses of 2 % He in Ar and pure He pulses flowing over H-ZSM-5. In contrast to CH₄, He pulses produce an endothermic peak which is followed by an equal exothermic heat effect, the value of it is about 30 % of the CH₄ effect. This can be explained by the fact, that Ar desorbs in the presence of He and is re-adsorbed again after the He pulse has passed the zeolite. Assuming that similar amounts of Ar are desorbed with CH₄ pulses, the measured heat effect has to be adjusted accordingly. The correction produces a heat of adsorption of 25.5 kJ/mole which agrees with the values obtained by gravimetry.

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