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Interactions of reactants in hydration of acetylene on Cd-zeolite catalysts

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Abstract

IR measurements were carried out with Cd-MFI and Cd-clinoptilolite at 25°C. Samples of different water content were contacted with acetylene at different pressures. Adsorbed acetaldehyde was formed from acetylene and water both adsorbed on similar $\text{Cd}^{2+}\text{Z}_2^-$ sites. The reaction between the two adsorbed reactants reveals the validity of Langmuir–Hinshelwood kinetics. Decrease of water content or increase of acetylene pressure facilitated the formation of carbonaceous deposits especially in the case of Cd-MFI. Deposits formed from acetylene displace adsorbed acetylene and acetaldehyde.

Keywords: Adsorption; Acetylene; Water; Surface reaction; Deposits

1. Introduction

The hydration of acetylene is catalysed by late transition metal ions (LTMI). Zeolites containing LTMI located in cationic sites were found favourable catalysts [1,2]. Having got a deeper insight into the mechanism the reaction seems suitable for testing LTMI-zeolite catalysts. The specific activity of cations as well as secondary transformations, such as crotonic condensation of product acetaldehyde and formation of carbonaceous deposits were shown to depend on the zeolite matrix [3].

The main process is a bimolecular surface reaction between water and acetylene, both adsorbed on similar cationic sites, i.e., on $\text{M}^{2+}\text{Z}_2^-$ [4,5].

Zeolite catalysts containing easily reducible LTMI, such as Cu^{2+} , Ag^+ , Hg^{2+} deactivate fast

[6]. Among zeolites containing non-reducible Cd^{2+} , Zn^{2+} , Pb^{2+} ions the Cd-zeolites are the most active [6]. They lose, however, 70–90 percent of the initial activity within 5 to 60 min because of residue formation, thereafter deactivation becomes slow. In this respect Cd-MFI and Cd-clinoptilolite show exceptional catalytic properties. Deactivation of Cd-MFI is much slower than that of other zeolites, while Cd-clinoptilolite retains practically its initial activity for several hours [7]. At room temperature the reaction of acetylene and the zeolitic water of the catalyst results in adsorbed acetaldehyde and secondary products [6]. At this temperature the formation of surface species is rather slow and can easily be followed by IR spectroscopy. Present IR study suggests that reaction occurs between adsorbed reactants, supporting the Langmuir–Hinshelwood kinetics reported ear-

lier [4,5] and indicates the effects and nature of by-products providing further information on surface reactions.

2. Experimental

2.1. Materials

The clinoptilolite (C,HEU) obtained from the natural occurrence of Horseshoe Dam, AZ, USA was of 95% mineral purity. The MFI zeolite was manufactured by Danube Refinery, Hungary. Powdered zeolites were ion-exchanged with 0.1 M CdCl₂ solution 5 times, for 8 h each, under refluxing. Compositions were: for Cd-C,HEU Si/Al = 4.5, Cd²⁺ = 1.4 meq/g; for Cd-MFI Si/Al = 31.7, Cd²⁺ = 0.3 meq/g.

Acetylene was obtained from a high purity Dissous gas (ODV, Hungary) by passing the gas through a trap at -77°C for removing acetone.

2.2. Methods

Self-supporting zeolite pellets with 4–7 mg/cm² thickness were placed in a vacuum cell for IR investigation. Samples were pretreated in vacuum for 1 h at different temperatures (*T_p*), then contacted with acetylene at room temperature and various pressures (*p_A*). After different contact times spectra were recorded in the range of 1200–4000 cm⁻¹ using a Nicolet 5PC FTIR spectrometer after different contact times.

IR spectra of acetaldehyde and crotonic aldehyde adsorbed on Cd-MFI and Cd-C,HEU pellets were determined and the characteristic bands were assigned. Accordingly, ν_{C=O} band of adsorbed acetaldehyde (AA,a) on Cd-MFI is at 1697 cm⁻¹, on Cd-C,HEU at 1711 and 1698 cm⁻¹. Bands of adsorbed crotonaldehyde (CA,a) on Cd-MFI or Cd-C,HEU can be detected at 1656 and 1637 cm⁻¹. For CH₃ both in AA,a and also for CA,a δ_{CH,asym} and δ_{CH,sym} are at 1414 and 1354 cm⁻¹, respectively, i.e. close to the gas phase frequencies [8,9].

3. Results and discussion

Cd-MFI was pretreated at 200°C, Cd-C,HEU at 100°C and 200°C. After these pretreatments the zeolite water content was appropriate for formation of AA,a in well detectable concentrations. Spectra of adsorbed products are shown in Figs. 1 and 2. The ν_{C=O} band at 1697 cm⁻¹ and the δ_{CH,sym} band at 1354 cm⁻¹ are assigned to AA,a on Cd-MFI (Fig. 1) [10]. The intensity of the bands passes through a maximum with increasing *p_A*. The ν_{C=O} band at 1711 cm⁻¹ and the δ_{CH,asym} at 1414 cm⁻¹ or δ_{CH,sym} at 1354 cm⁻¹ are assigned to AA,a on Cd-C,HEU (Fig. 2) [10]. The intensity of the bands shows monotonous increase. After 4-h contact time carbonaceous deposits were formed on the Cd-MFI as indicated in Fig. 1 by the bands of conjugated polyenes at 1604 cm⁻¹ [11] and by bands at 1570, 1508 cm⁻¹ characteristic for the aromatic C–C stretching vibration in carbon residues [12,13]. On Cd-C,HEU in Fig. 2 product AA,a only is observable. In the case of Cd-MFI the increasing pressure of acetylene

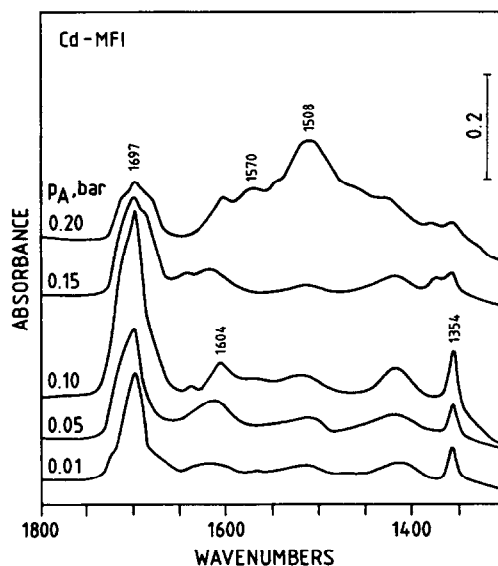


Fig. 1. Absorption spectra of surface species formed on Cd-MFI after contacting with acetylene for 4 h at different pressures (*p_A*) at 25°C. The spectrum of samples pretreated at 200°C is subtracted.

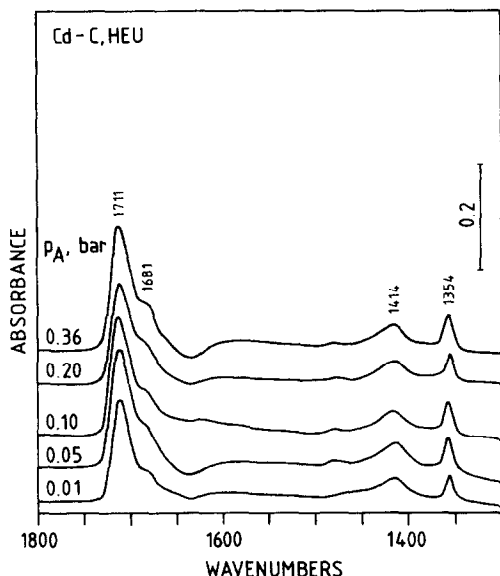


Fig. 2. The same as Fig. 1 but for Cd-C,HEU pretreated at 100°C.

results first in an increase of (AA,a) then an increase of carbonaceous deposits which seem to displace partly AA,a. Crotonic condensation causing deactivation at higher temperatures [6] seems to play a minor role at 25°C.

In order to obtain more accurate information on the activities at different p_A , initial rates of formation of AA,a were determined as follows. The absorbances of AA,a at 1697 cm^{-1} for Cd-MFI and at 1711 cm^{-1} for Cd-C,HEU were determined as heights of the absorption band in absorbance arbitrary unit divided by the thickness of the pellet in mg/cm^2 and plotted against the contact time with acetylene. Initial slopes of fitted curves were assumed to be proportional to the initial rates of AA,a formation, $r_{AA,a}^0$ in $[\text{a.u.}] \text{cm}^2 \text{mg}^{-1} \text{h}^{-1}$. $r_{AA,a}^0$ are plotted as a function of p_A (Fig. 3). Correlations are in accordance with the qualitative conclusions drawn from the changes in spectra (Figs. 1 and 2), i.e., $r_{AA,a}^0$ passes through a maximum for Cd-MFI while for Cd-C,HEU pretreated at 100°C, it increases monotonously with p_A .

The intensity of the $\nu_{\equiv\text{C}-\text{H,asym}}$ bands at 3242 cm^{-1} for Cd-MFI and at 3207 cm^{-1} for Cd-C,HEU was used to characterize the concentration of the adsorbed acetylene (A,a). The corre-

sponding band of the gas-phase acetylene is at 3285–3290 cm^{-1} . On adsorption over LTMI the frequency decreases [14,15]. The adsorbed amounts proportional to the band intensities are expressed in $[\text{a.u.}] \text{cm}^2 \text{mg}^{-1}$ units. The $\nu_{\text{C}=\text{C}}$ stretching vibration bands appear around 1950 cm^{-1} becoming IR active upon adsorption [10]. These bands were not used to measure the surface concentrations of A,a because they are essentially weaker than the $\nu_{\equiv\text{C}-\text{H,asym}}$ bands. (Because of small amounts A,a could not be determined gravimetrically.) (A,a) plotted as a function of p_A are also shown in Fig. 3 (dotted curves). $r_{AA,a}^0$ and (A,a) change similarly, for Cd-C,HEU pretreated at 100°C both increase with p_A , whereas for Cd-MFI and Cd-C,HEU pretreated at 200°C both pass through maxima. Enhanced dehydration of Cd-C,HEU results in lower $r_{AA,a}^0$ and somewhat higher (A,a). These findings suggest that adsorbed acetylene is involved in the hydration to acetaldehyde.

The decrease of (A,a) and $r_{AA,a}^0$ after maxima is due to deposits (see in Fig. 1) formed probably from acetylene at higher p_A values. The appearance of bands assigned to conjugated polyenes (at 1604 cm^{-1}) and aromatics (bands at 1570 and 1508 cm^{-1}) substantiate that deposits are acetylene derivatives.

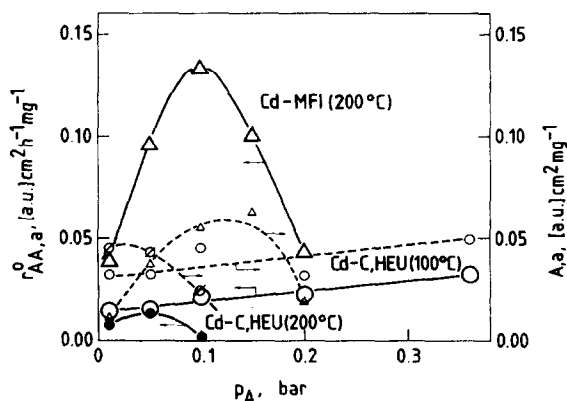


Fig. 3. Initial rate of formation of adsorbed acetaldehyde, $r_{AA,a}^0$, (solid curves; Δ , \circ , \bullet) and the amount of adsorbed acetylene (A,a) (dotted curves; Δ , \circ , \emptyset) after contacting for 1 h with acetylene at different pressures (p_A) for Cd-MFI (Δ , Δ) and Cd-C,HEU (\circ , \circ and \bullet , \emptyset) after pretreatments at 100°C and 200°C, respectively).

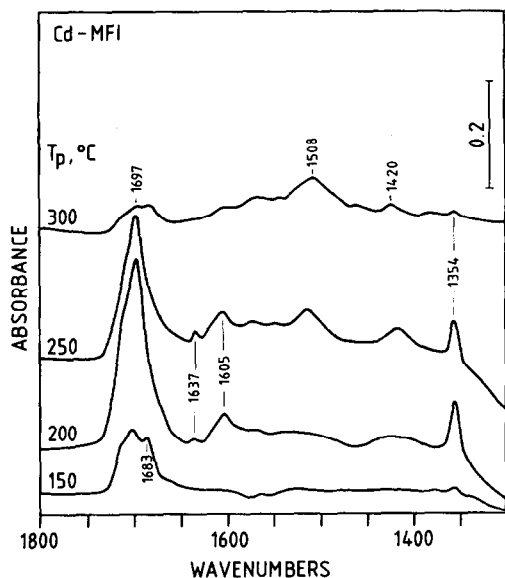


Fig. 4. Absorption spectra of surface species formed on Cd-MFI pretreated at different temperatures for 1 h in vacuum then contacting with acetylene at 0.1 bar and 25°C for 4 h. The spectrum of pretreated samples is subtracted.

The concentration of water, the other reactant, was varied by T_p . Acetylene was contacted with the two Cd-zeolites dehydrated to different degrees. Spectra of the surface species formed are shown in Figs. 4 and 5. At higher T_p deposit

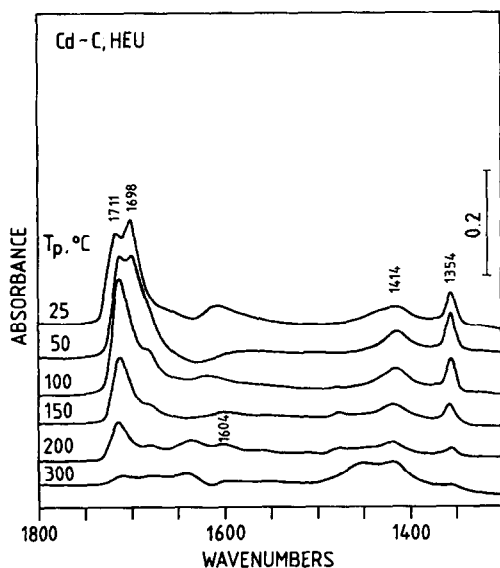


Fig. 5. The same as Fig. 4 but for Cd-C,HEU.

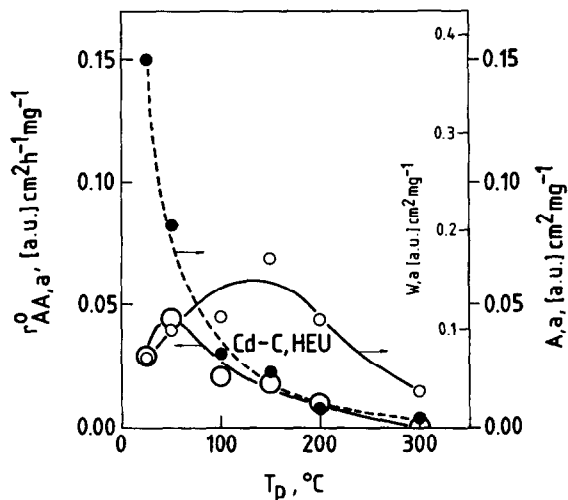


Fig. 6. Initial rate of formation of adsorbed acetaldehyde, $r_{AA,a}^0$ (○), initial water content (W, a) (dotted curve, ●) and adsorption of acetylene (A, a) (◊) at 0.1 bar after 1 h contacting over Cd-C,HEU as a function of pretreatment temperature (T_p).

formation on Cd-MFI is considerable. Absorption bands of AA,a are observable at 1711, 1697, 1683 cm^{-1} with intensities depending on the water content of the catalysts. The bands can be assigned to AA,a on different sites [6,9,16]. Following the intensity change of the characteristic IR bands, it can be concluded that surface concentration of AA,a passes through a maximum with increasing T_p .

Initial rates, $r_{AA,a}^0$, amounts of A,a were determined for samples pretreated at different temperatures as done before when p_A was varied. Water content (W,a) was regarded to be proportional to the δ_{water} band absorbances at 1630 cm^{-1} [17] right after pretreatment and before contacting with acetylene. All these data are plotted against T_p for Cd-C,HEU in Fig. 6. (The water concentration in Cd-C,HEU decreases from 140 mg/g to 50 mg/g between 100 and 300°C on the basis of thermogravimetric measurements.)

(W,a) monotonously decreases, (A,a) passes through a maximum, $r_{AA,a}^0$ also does but at lower T_p . The course of the three curves roughly reflects the kinetic relations [4,5]: $r_{AA,a}^0$ is proportional to the product of (A,a) and (W,a).

When T_p is lower than 150°C, the amounts of A,a and W,a show opposite changes reflecting a partition of adsorption on similar sites as it follows from the kinetics, too.

The decrease of (A,a) and $r_{AA,a}^0$ at higher pretreatment temperatures may be ascribed to structural destruction of C,HEU above 200°C [7]. Namely, increased deposit formation on Cd-C,HEU because of low water contents seems unlikely (Fig. 5).

Clear correlations for Cd-MFI could not be established. When low T_p s (< 150°C) were applied, AA,a was formed in small amounts which could not reliably be detected. After higher-temperature pretreatments (> 200°C) the large amounts of carbonaceous deposits formed (see in Fig. 4) caused confusing situation.

The zeolite media was found to affect strongly the catalytic behaviour of the Cd^{2+} sites [3,7,10]. The hydration of acetylene takes place between reactants adsorbed on similar $Cd^{2+}Z_2^-$ sites [4,5]. Probably the different coordination of Cd^{2+} in C,HEU [18] and MFI [19] is responsible for the differences shown in Figs. 3 and 6: (i) at similar acetylene coverage Cd-MFI shows higher hydration activity; (ii) maximum of $r_{AA,a}^0$ depending on the degree of dehydration appears at higher water content on Cd-C,HEU than on Cd-MFI (because of uncertainties not plotted in Fig. 6), and (iii) Cd-MFI is more susceptible to formation of carbonaceous deposits.

4. Conclusions

The hydration of acetylene to acetaldehyde on Cd-zeolite catalysts takes place according to the Langmuir–Hinshelwood kinetics through rate determining surface reaction between adsorbed water and acetylene [4,5]. This mechanism evaluated on the basis of steady-state kinetic data determined at 180°C could be verified by IR spectroscopic investigations of surface species at temperature (25°C) where steady-state cannot prevail and the transformations are essentially slower. It has been found that: (i) at

constant water coverage the formation rate of adsorbed acetaldehyde changes similarly as the surface concentration of acetylene; (ii) the amount of adsorbed acetylene and water changes in opposite direction indicating adsorption on similar sites; (iii) adsorption of water and formation rate of adsorbed acetaldehyde do not simply correlate because, on the one hand, the concentration decrease of adsorbed water permits increased formation rate of adsorbed acetaldehyde, on the other hand, the decreasing concentration of reacting water results in decreasing formation rate of adsorbed acetaldehyde; (iv) decrease of water content, similarly the increase of acetylene pressure favours the formation of carbonaceous deposits which suppress the adsorption of acetylene and product acetaldehyde. At 25°C deposits are formed mainly from acetylene and not from crotonaldehyde as found at 180°C [6]. All these correlations agree qualitatively for Cd-MFI and Cd-C,HEU but the quantitative differences are considerable for these two catalysts.

The IR spectroscopic results support the kinetic conclusions and supplementary information, not accessible from the kinetics, could be obtained.

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