Acetylene-Hydration Kinetics on Cadmium-Exchanged Clinoptilolite Catalyst

Preliminary Communication

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Hydration of acetylene under steady-state conditions around 450 K proceeds on Cd-clinoptilolite without catalyst deactivation and formation of by-products. Reaction rates were determined under steady-state conditions at different partial pressures of acetylene, water, and acetaldehyde. In relation with the results, rate equations for different kinetic models were evaluated. *Langmuir-Hinshelwood* kinetics was established. According to this model, acetylene and water must adsorb on similar sites, and the surface reaction between the adsorbed reactants is the rate-determining step, which is followed by equilibrated desorption of the produced acetaldehyde.

Introduction. – In the hydration of acetylene around 450 K under steady-state conditions, late-transition-metal ions, such as Cu^{2+}, Ag^{+}, Zn^{2+}, Cd^{2+}, and Hg^{2+}, were found to be catalytically more active in cationic sites of zeolites than in oxides, phosphates, tungstates, or molybdates [1]. The Cu-, Ag-, and Hg-zeolites deactivated fast due to the reduction of the metal ions by acetylene to inactive metals [2]. However, deactivation was also observed for the nonreducible Cd- and Zn-zeolites. The activity of Cd-exchanged X-zeolite, Y-zeolite, and mordenite monotonously decreased by 15, 30, and 40% per hour, respectively, because of the formation of a carbonaceous deposit. In contrast, a zeolite Cd-clinoptilolite catalyst preserved its relatively high initial activity for several hours. The reaction proceeded without formation of by-products [2].

The catalyst was prepared from clinoptilolite-containing sedimentary rock. In such rocks, the clinoptilolite is accompanied by different mineral constituents. The catalytic effect of the non-zeolitic mineral components was suggested to be insignificant since the activity of the rock was proportional to the clinoptilolite content [3].

Previous IR studies of Cd-zeolites [4][5] suggested that adsorbed acetylene is bound to the Cd^{2+} ions in different forms. One of the forms, namely the cadmium acetylide, seemed to be active in hydration. In addition, the formation of adsorbed acetaldehyde was found to be proportional to the amount of adsorbed water. The water bound to the Cd^{2+} ions in heterolytically dissociated form competed with the acetylene for the adsorption sites. These experimental findings suggested that the reaction proceeds at room temperature (as used in the IR measurements) between reactants bound to Cd^{2+} ions. The question then arises whether the same mechanism prevails at higher temperatures, such as between 393 and 453 K, under steady-state reaction conditions. The present work is an attempt to answer this question on the basis of reaction kinetics obtained with Cd-clinoptilolite as a catalyst.

Experimental Part

Materials. The natural zeolite clinoptilolite used in this study was a volcanic tuff from Horseshoe Dam, Arizona, USA. A clinoptilolite content of 96 wt-% was determined from the adsorption capacity for CO_2 [6]. The Si/Al ratio was 4.5, the cation-exchange capacity 2.37 mequiv./g, and the ignition loss 14.1 wt-%. A powdered sample (30 g) was treated by ion-exchange 5 times, (8 h each) under reflux in the presence of 200-ml portions of 0.1M $CdCl_2$. The ion-exchange degree, (Cd/2Al) · 100, was 58%, *i.e.*, the sample contained 7.7 wt-% cadmium. The Cd-exchanged material was recovered by filtration, dried, and compressed into pellets without binder. The pellets were crushed and sieved. The fraction of 0.6 – 1.0 mm was used.

Pure acetylene was obtained from a flow of 'Dissous gas' (product of *ODV*, Hungary) by trapping acetone at 195 K (the term 'Dissous gas' refers to the gas obtained from a tank containing acetylene absorbed in acetone supported on pumice.)

The acetaldehyde ('zur Synthese' grade) of *Merck*, Germany, was used.

Methods. A conventional flow-through reactor was used at 100 kPa total pressure. The reaction system was equipped with feeding accessories for acetylene, water, acetaldehyde, and N_2. The unconverted water, containing dissolved acetaldehyde product, was condensed by cooling the reactor output to room temperature and separated from the gas phase. The gaseous effluent of the condenser consisted of carrier N_2, unconverted acetylene, and acetaldehyde vapor. The amount and composition of the liquid and gaseous streams were determined. A perfect material balance was found between the feed and the reactor effluents. Conversions (c) were calculated by dividing the amount of product acetaldehyde (in mol) leaving the reactor by the amount of acetylene (in mol) fed during the same period of time.

The initial partial pressures of acetylene ($p_A{}^o$), water ($p_W{}^o$), and acetaldehyde ($p_{AA}{}^o$) in the feed and the space-time of acetylene, $\tau = w_{cat}/F$ (w_{cat} = weight of catalyst/g_{cat}; F = feed rate of acetylene/$mol_A\ s^{-1}$) were varied. Conversions at given initial partial pressures and temperature were plotted against space-time. The slopes of the conversion curves are equal to the rates of reaction under the applied conditions. The actual partial pressures p_A, p_W, and p_{AA} can be calculated from the initial partial pressures $p_A{}^o$, $p_W{}^o$, the actual conversion c, and the mol-fraction $x_A{}^o$ of acetylene in the feed by *Eqns. 1* and *2*, and, provided that acetaldehyde is not fed ($p_{AA}{}^o = 0$), by *Eqn. 3*, respectively.

$$p_A = (1 - c)p_A{}^o/(1 - c\, x_A{}^o) \tag{1}$$

$$p_W = (p_W{}^o - c\, p_A{}^o)/(1 - c\, x_A{}^o), \tag{2}$$

$$p_{AA} = c\, p_A{}^o/(1 - c\, x_A{}^o) \tag{3}$$

Results and Discussion. – Two series of measurements were carried out. In the first series, the temperature was 413 K; $p_A{}^o$ was increased to 33 kPa at constant $p_W{}^o = 67$ kPa (*Conditions A*), $p_W{}^o$ was varied between 17 and 83 kPa, while $p_A{}^o = 17$ kPa (*Conditions B*), and, at $p_A{}^o = 17$ kPa and $p_W{}^o = 67$ kPa, $p_{AA}{}^o$ was varied in the range 0.15 to 2.5 kPa (*Conditions C*). The total pressure was maintained at 100 kPa by admixing N_2. Initial reaction rates (r_o) were determined at $\tau = 0$ with a reliability of ± 2%. Results are shown in *Fig. 1,a – c*.

In the second series of measurements, experiments were carried out at 393, 413, 433, and 453 K at $p_A{}^o = 33$ kPa, $p_W{}^o = 67$ kPa, and $p_{AA}{}^o = 0$. Conversion curves are shown in *Fig. 2*. For the sake of brevity, only the reaction rates determined at different conversions at 413 K are summarized in the *Table*.

Fig. 1 demonstrates that the initial reaction rate r_o is proportional to the partial pressure of acetylene and shows negative order in water and acetaldehyde. The experimental data were evaluated with different tentative kinetic models taken into account. The following cases were considered:

Case 1: Langmuir-Hinshelwood kinetics, where it is assumed that the rate-determining process step is the adsorption of *a*) the acetylene or *b*) the water, *c*) is the surface reaction between the adsorbed reactants, or *d*) is the desorption of the acetaldehyde product;

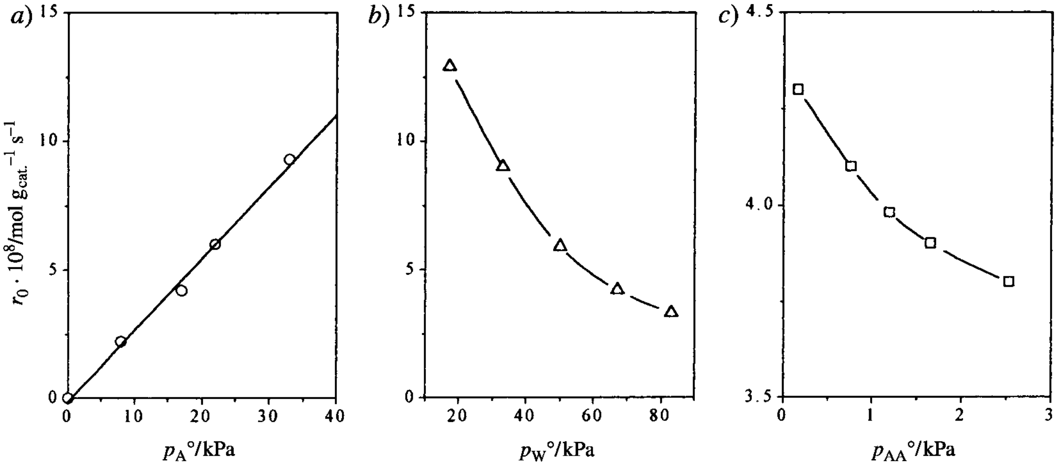

Fig. 1. *Initial rate* r_o *of acetylene hydration on Cd-clinoptilolite at 413 K as a function of* a) *partial pressure of acetylene* (*Conditions A:* $p_W° = 67$ kPa, $p_{AA}° = 0$ kPa), b) *of partial pressure of water* (*Conditions B:* $p_A° = 17$ kPa, $p_{AA}° = 0$ kPa), *and* c) *of partial pressure of acetaldehyde* (*Conditions C:* $p_A° = 17$ kPa, $p_W° = 67$ kPa).

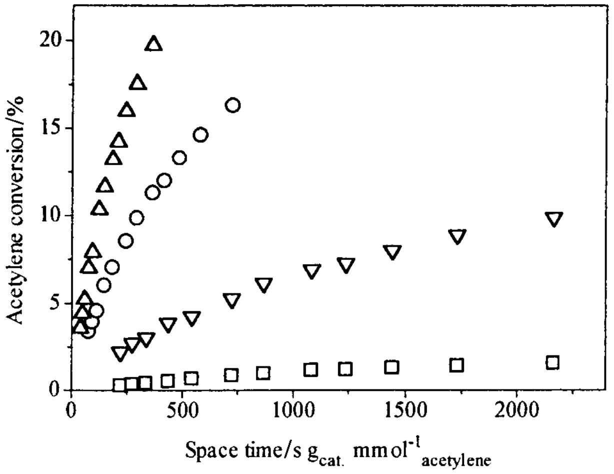

Fig. 2. *Conversions of acetylene hydration on Cd-clinoptilolite at 393 K* (□), *413 K* (▽), *433 K* (○), *and 453* (△) *as a function of space-time.* The initial partial pressures for acetylene and water are 33 and 67 kPa, respectively.

Table. *Reaction Rates at Different Conversions.* Conditions: $T = 413$ K, $p_A° = 33$ kPa, $p_W° = 67$ kPa, feed rate of acetylene = 20–200 ml/min, and amount of catalyst Cd-clinoptilolite = 30 g

Conversion *c*/%	2	3	4	4.5	5	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10
Reaction rate/mol/$g_{cat}s \cdot 10^8$	8.8	7.3	6.3	5.8	5.2	4.7	4.3	4.0	3.7	3.4	3.1	2.7	2.5	2.4	2.2

Case 2: Rideal-Eley kinetics, where it is assumed that the rate-determining process step is *a*) the adsorption of acetylene, *b*) the surface reaction between adsorbed acetylene and gas phase water, or *c*) product desorption. Alternatively, the rate-

determining step is *a*′) the adsorption of water, *b*′) the surface reaction between adsorbed water and gas phase acetylene, and *c*′) the product desorption.

Rate equations were derived for all of these tentative cases, and two of them permitted rate functions to be written in accordance with the results shown in *Fig. 1*, *i.e.*, first-order kinetics in acetylene and negative order both in water and acetaldehyde, namely *Case 1a*, when the reaction takes place between adsorbed reactants and the rate of acetylene adsorption controls the rate of the reaction (see *Eqn. 4*), and *Case 1c*, when the rate of the surface reaction controls the reaction rate (see *Eqn. 5*).

$$r = k_A p_A \, (1 + K_W \, p_W + K_{AA} p_{AA})^{-1} \tag{4}$$

$$r = k \; K_A p_A \; K_W \, p_W \, (1 + K_A p_A + K_W \, p_W + K_{AA} p_{AA})^{-2} \tag{5}$$

In *Eqns. 4* and *5* k and k_A stand for the rate constant of the surface reaction and the adsorption rate constant of acetylene, respectively. K_W, K_{AA}, and K_A represent adsorption equilibrium constants for water, acetaldehyde, and acetylene. The kinetics according to *Case 1c* can be first-order in acetylene if the term $K_A p_A$ in the denominator is negligible due to a weak acetylene adsorption.

Eqns. 4 and *5* can be transformed into the linear forms given by *Eqn. 6* and, after neglecting the term $K_A p_A$, by *Eqn. 7*, respectively.

$$p_A / r = 1/k_A + K_W \, p_W / k_A + K_{AA} \, p_{AA} / k_A \tag{6}$$

$$(p_A \, p_W / r)^{1/2} = 1/(k \; K_A \; K_W)^{1/2} + K_W \, p_W / (k \; K_A \; K_W)^{1/2} + K_{AA} p_{AA} / (k \; K_A \; K_W)^{1/2} \tag{7}$$

Plotting the initial rates from *Fig. 1,b* against $p_W{}^{o}$ according to *Eqns. 6* and *7*, a linear correlation is found with *Eqn. 7* only (*Fig. 3,b*). Considering a larger conversion range and by substituting *Eqs. 1–3* into *Eqn. 6* or *7*, one obtains *Eqn. 8* and *9*, respectively.

$$(1 - c) p_A{}^{o} / r = \alpha + \beta \; c \tag{8}$$

where $\alpha = 1/k_A + K_W \, p\mathrm{W}^{o} / k_{A \text{ and}} \beta = K_{AA} p\mathrm{A}^{o} / k_A - K_W \, p\mathrm{A}^{o} / k_A - x_A{}^{o} / k_A$

$$[(1 - c)(p_W{}^{o} - c \; p_A{}^{o}) p_A{}^{o} / r]^{1/2} = \gamma + \delta \; c \tag{9}$$

where $\gamma = (1 + K_W \; p_W{}^{o}) / (k \; K_A \; K_W)^{1/2}$ and $\delta = (K_{AA} \; p_A{}^{o} - K_W \; p_A{}^{o} - x_A{}^{o}) / (k \; K_A \; K_W)^{1/2}$

On plotting $(1 - c) p_A{}^{o} / r$ and $[(1 - c)(p_W{}^{o} - c \; p_A{}^{o}) p_A{}^{o} / r]^{1/2}$ against c (*e.g.*, from the data in the *Table*), a linear correlation could be verified again for the second case (see *Fig. 4*), *i.e.*, with *Eqn. 7*, indicating that the kinetic model of *Case 1c* is not in contradiction with the experimental data. However, the constants involved in *Eqn. 5* can not be determined since K_A and k are not separable, and the intercept in *Fig. 3,b* is nearly zero indicating that $1/(k \; K_A K_W)^{1/2}$ is negligible in *Eqn. 7*. Thus, the absolute values of K_W and K_{AA} can not be calculated either. Only the K_W / K_{AA} ratio can be determined by dividing the slope of the line in *Fig. 3,b* by that in *Fig. 5*, as it follows from *Eqn. 7*. Accordingly, $K_W / K_{AA} = 0.7 \pm 0.05$ at 413 K. Inhibition by the product acetaldehyde is to be expected at higher conversions.

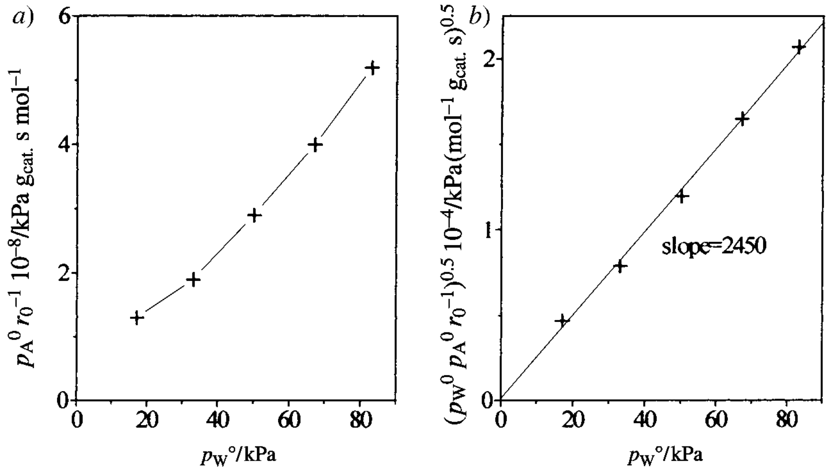

Fig. 3. *Representation of the data of* Fig. 1,b *according to* a) *Eqn. 6 and* b) *Eqn. 7.*

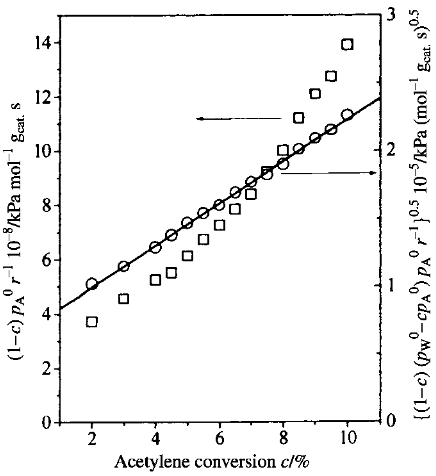

Fig. 4. *Representation of* r = *f*(c) *function according to* Eqns. 8 *and* 9. Pairs of *r* and *c* values were determined at 413 K.

At any rate, the kinetics is in agreement with the mechanism suggested by our previous IR study [5]. Accordingly, the surface reaction takes place between water and acetylene, both adsorbed at similar Cd^{2+} sites. The composition of the catalyst indicates that, as an average, nineteen TO_4 tetrahedra belong to each Cd^{2+} ion (T designates the framework Al- or Si-atom). Thus, the distance between Cd^{2+} sites could be too large to permit molecular interaction between Cd^{2+}-bound species, if the distribution of Cd^{2+} ions was entirely uniform. It was reported [7] that the Cd^{2+} ions are preferentially located near the center of ten and eight-membered rings in clinoptilolite. Since such rings are in close vicinity, the presence of Cd^{2+} ion pairs seems likely.

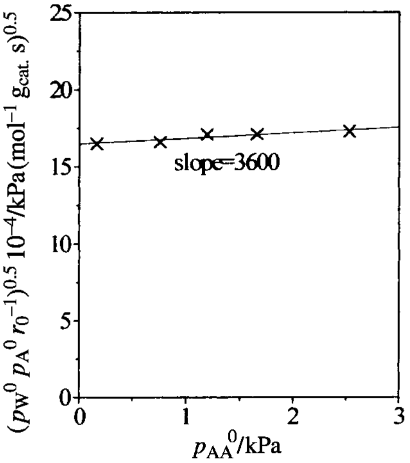

Fig. 5. *Representation of the data of* Fig. 1,c, *according to* Eqn. 7.

Conclusions on the type of adsorption were drawn from the IR results, whereas the rate-determining surface reaction between the adsorbed reactants was evidenced from the kinetics. It is to be noted that kinetics describing a process where two different molecules adsorbed at the same type of surface centers react with each other, is rather exceptional in zeolite catalysis.

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