

Gravimetric Study of the Dynamics of Adsorption, Desorption, and Polymerization of Propene on γ -Alumina*

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The dynamics of adsorption and desorption of propene on γ -alumina has been studied by means of Cahn recording microbalances at temperatures between 180 °C and 380 °C. It was observed that only a part of propene is adsorbed strongly, whilst the rest is weakly adsorbed. The amount of adsorbed propene first decreases with increasing temperature, but, starting from about 300 °C, this behaviour changes markedly, yielding again the higher extent of adsorption. A model of the process involving propene adsorption followed by its dimerization inside the sorbent pores has been suggested and tested by simulation and fitting.

When a stream of alkylamine vapour flows over the layer of γ -alumina heated to temperatures above 300 °C, catalytic deamination occurs. After stopping the reactant feed, the temporary increase of the reaction rate was observed [1]. This phenomenon, the so-called stop-effect, has been a subject of several studies [2–8]. Based on the assumption that alkylamine is adsorbed on two different kinds of alumina adsorption sites, a hypothesis that the deamination occurs only when the alkylamine molecule is bound to both types of sites simultaneously, has been suggested. The stop-effect is then explained as a result of competition of the alkylamine molecules bound only by one of their ends with those bound by both ends.

In our earlier study [9] of propylamine adsorption and reaction on γ -alumina using Cahn recording microbalance technique we confirmed that propylamine is adsorbed on two different kinds of adsorption sites. In this study, the above-mentioned stop-effect was observed, too. We found that the amount of propene produced by this reaction increases after switching the feed off. Surprisingly, the propylene production ceased much earlier than the catalyst sample could attain its original mass measured prior the adsorption step. We suggested the mechanism of this phenomenon based on the competition of the reaction products, namely ammonia and propene. Later on, we studied the dynamics of adsorption and desorption of ammonia on γ -alumina experimentally, using the same gravimetric technique [10]. A mechanism assuming the adsorption of ammonia molecule on both the acidic and basic

Lewis sites was suggested. A successful fit of the experimental data proved the model validity.

The purpose of the present paper is to investigate the adsorption behaviour of propene, the second product of the deamination reaction on γ -alumina, using the same experimental technique, the gravimetry, as it was employed in our previous studies. For the description of the process, the model is suggested and it is shown how it can be used for deconvolution of gravimetric results, which represent the summation of individual contributions of adsorbed species.

EXPERIMENTAL

Adsorbent

Commercial γ -alumina catalyst pellets (CHEROX 33-00, Chemical Works Litvínov) were crushed and the fraction with the size of 0.2–0.4 mm of this adsorbent was used in the experiments. Its BET surface area was 243 m² g⁻¹, the most frequent pore radius was 122 nm.

Procedure

The adsorption and desorption measurement of propene on γ -alumina was performed using the recording microbalances CAHN D-200. The measuring range up to 150 mg was used, ensuring the measurement precision of 0.1 μ g. The initial sample mass of alumina was chosen near the maximum of the range, typ-

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ically about 130 mg. The temperature of the sample was measured by the thermocouple type K positioned close to the sample pan in a sample tube of balances. All gases were introduced into the balances in the upstream direction. The mass and temperature data *vs.* time were recorded by personal computer with sampling frequency of 10 s.

The activation of the sorbent was performed as described elsewhere [9]. After the sorbent activation in argon, the adsorption of propene at given temperature was started by switching from the argon flow to pure propene at a rate of $1.13 \text{ dm}^3 \text{ h}^{-1}$. After 3 h of adsorption, the desorption was started by replacing propene by pure argon at a flow rate of $4.45 \text{ dm}^3 \text{ h}^{-1}$. The isothermal part of desorption lasted 2 h. Then, the TPD (temperature programmed desorption) experiment with the temperature upper limit of 450°C and the heating rate of 2°C min^{-1} was performed in a stream of pure argon.

RESULTS AND DISCUSSION

The adsorption and desorption of propene was studied at several temperatures. Each experimental run consisted of isothermal adsorption and desorption followed by temperature programmed desorption. The experimental data are given in Fig. 1. It was observed that propene adsorption is first quick, and then it slows down, but apparently even after 3 h it does not reach the adsorption equilibrium. During isothermal desorption step, only a part of propene adsorbed is removed within 2 h. This behaviour resembling that of ammonia and propylamine indicates that also in the case of propene both the weak and strong adsorption sites have to be taken into account.

The behaviour of propene at temperatures below 300°C differs from that at higher temperatures: while below this value the adsorbed amount of propene after 3 h decreases with increasing adsorption temperature, above this value the rise of temperature increases the amount of propene adsorbed. Also the

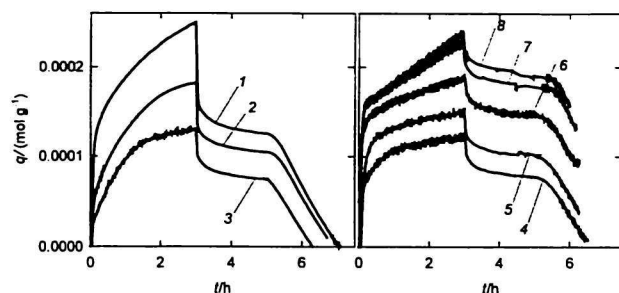


Fig. 1. Adsorption and desorption of propene at constant temperatures, followed by TPD. Temperatures of isothermal part of the run: 1. 180°C ; 2. 230°C ; 3. 280°C ; 4. 300°C ; 5. 320°C ; 6. 340°C ; 7. 360°C ; 8. 380°C .

behaviour during the TPD part of the experimental run differs essentially. While at runs performed below the critical temperature the TPD leads to complete removal of adsorbed propene from the sorbent, above this temperature the even increasing proportion of propene is retained within the sorbent pores. This portion of propene is only removed by the sorbent re-activation in the presence of wet air. Usually, compounds of higher molecular mass, probably some propene oligomers, are produced under these conditions.

Based on analysis of the above-mentioned behaviour, the following model of propene adsorption was proposed. Propene P is supposed to adsorb primarily on alumina adsorption sites S



The adsorbed molecules are activated by adsorption, so that they might react with another molecule of propene, forming a dimer



The dimer itself may attain its own adsorption—desorption equilibrium



As the propylene polymerization occurs in a limited portion of γ -alumina pores, propagation of the reaction (B), leading to higher propene oligomers, is neglected at this stage of the model development. The model complexity was limited with the aim to keep the number of necessary kinetic parameters reasonably low and with respect to the extent of experimental results.

The kinetics of the above-mentioned chemical reactions is expressed by the following differential equations

$$\begin{aligned} \frac{d[\text{PS}]_s}{dt} = & k_1[\text{P}][\text{S}]_s - k_{b1}[\text{PS}]_s - \\ & - k_2[\text{P}][\text{PS}]_s + k_{b2}[\text{P}_2\text{S}]_s \end{aligned} \quad (1)$$

$$\begin{aligned} \frac{d[\text{P}_2\text{S}]_s}{dt} = & k_2[\text{P}][\text{PS}]_s - k_{b2}[\text{P}_2\text{S}]_s + \\ & + k_3[\text{P}_2][\text{S}]_s - k_{b3}[\text{P}_2\text{S}]_s \end{aligned} \quad (2)$$

$$\frac{d[\text{P}_2]}{dt} = -k_3[\text{P}_2][\text{S}]_s + k_{b3}[\text{P}_2\text{S}]_s \quad (3)$$

The concentrations of free and occupied adsorption sites on alumina surface are bound by mass balance

$$[\text{S}]_s = n_s - [\text{PS}]_s - [\text{P}_2\text{S}]_s \quad (4)$$

Total specific amount of substance of propene adsorbed on alumina sample is given by

$$q = [\text{PS}]_s + (M_2/M_1)[\text{P}_2\text{S}]_s \quad (5)$$

System of differential equations (1—3) together with

algebraic equations (4) and (5) and the conditions defining the propene concentration pulse (eqn (6))

$$0 < t < 3 \text{ h}, [P] = \text{const} > 0; t \geq 3 \text{ h}, [P] = 0 \quad (6)$$

was numerically solved using the initial conditions

$$t = 0, [PS]_s = [P_2S]_s = [P_2]_s = 0 \quad (7)$$

The model here suggested neglects the effects of both outer and inner diffusion. The effect of the outer diffusion (*i.e.* the diffusion of the adsorbate from the free flow of the gas into the layer of adsorbent particles) has been discussed earlier [11]. It was shown that this effect could be largely suppressed by choosing the gas flow rate high enough. Neglecting of this effect leads to lowered values of both k_i and k_{bi} rate constants. The ratio of these constants, k_i/k_{bi} , which equals equilibrium constant of the particular reaction, is influenced by outer diffusion effect even less. As concerns the inner diffusion (*i.e.* inside the pores of the adsorbent particles), its effect on slowing down the overall process can be considered to be negligible in comparison with the rate of adsorption, desorption, and reaction. It is so because of very short diffusion path inside the sub-millimeter adsorbent particles employed. This leads to very short time for reaching the diffusion equilibrium, especially when compared with the experimental data showing that even after three hours of adsorption the overall equilibrium was not established.

The above developed model was used to fit the experimental results shown in Fig. 1 using the software package Scientist version 2.01 for Windows, Micromath Research, U.S.A. Results of the curve fits, including the deconvolution to individual components given by eqns (1) to (3), are shown in Fig. 2. It may be observed that the model, albeit simplified, describes the experimental data quite acceptably. The results of deconvolution show that below 300 °C the formation of the dimer P_2S prevails in the adsorption stage of the experiment, and that the concentration of the monomer PS increases only after stopping the propene feed in the gas flow, obviously when more free adsorption sites became there available. Above 300 °C, the situation changes: more and more of adsorbed monomer is present even at the adsorption stage of the experiment, because the competition on free adsorption sites is suppressed by evolving more and more of propene dimer into the gas phase.

The coefficient of variations of the fits of seven model parameters involved ($k_1 \dots k_{b3}$ and n_s) scarcely exceeded few tens %. The rate constants values k_i , k_{bi} were used for calculation of equilibrium constants K_A , K_B , and K_C of corresponding reactions. The results obtained are given in Fig. 3. It may be observed that, within temperature range investigated, the data on equilibrium constants obey the Arrhenius law quite well. During the fitting process, the maximum concen-

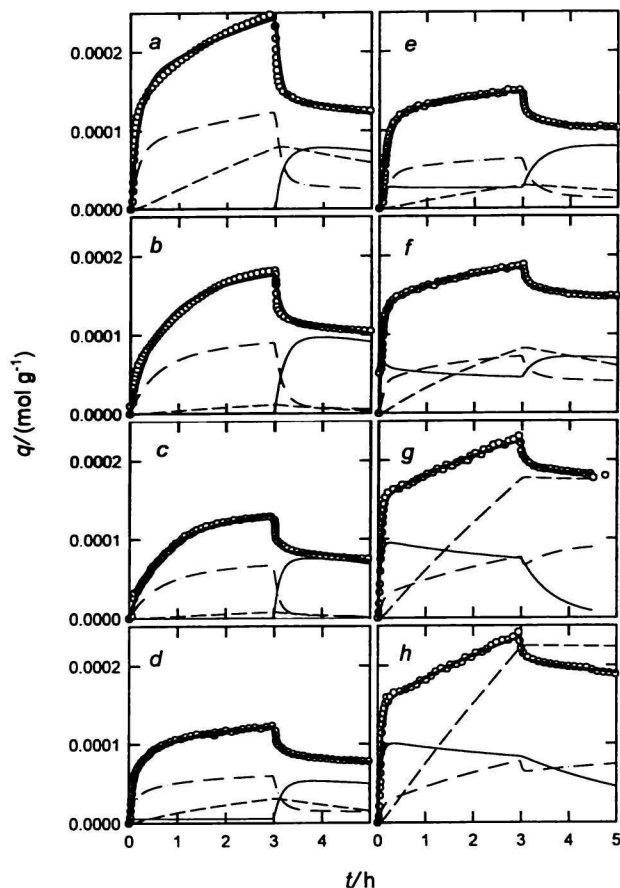


Fig. 2. Fitting and deconvolution of the model to experimental data: thick solid line – q calculated; thin solid line – $[PS]_s$; dotted dashed line – $[P_2S]_s$; dashed line – $[P_2]$ (values divided by 10); circles – experimental points. Temperatures of isothermal part of the run: a) 180 °C; b) 230 °C; c) 280 °C; d) 300 °C; e) 320 °C; f) 340 °C; g) 360 °C; h) 380 °C.

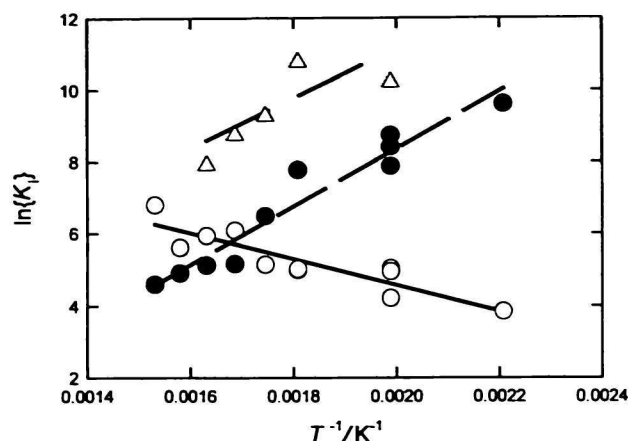


Fig. 3. Arrhenius plots of equilibrium constants: open circles – K_A ; full circles – K_B ; triangles – K_C . Lines represent least-square estimates of straight lines going through the points.

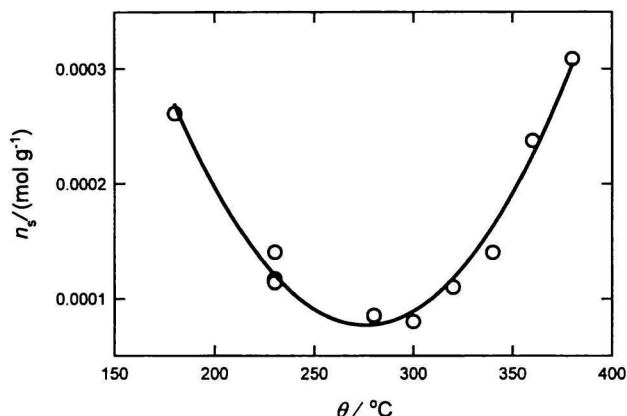


Fig. 4. The effect of adsorption temperature on the maximum concentration adsorption sites, n_s , as fitted by the model. The line represents the best fit of quadratic equation to the points.

trations of sites suitable for propene adsorption, n_s , were also calculated. These values remarkably correlate with the amount of propene adsorbed during the isothermal parts of the experimental runs, cf. Fig. 1 and Fig. 4.

The model here suggested is by no means conclusive. It does not reflect, for instance, the existence of at least two kinds of adsorptive sites in γ -alumina and thus the possibility of propene being bound to them. Moreover, only a part of adsorbed propene might be activated for subsequent dimerization. And, last but not least, the reaction may propagate further, by forming trimer of monomer units. (Higher degree of polymerization seems to be less feasible in the limited diameter of alumina pores.) The experimental data were fitted also with models reflecting these features. Any model refinement, however, increases the number of fitted parameters, thus making their values more uncertain.

SYMBOLS

k_1, k_3	component adsorption rate constants	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
k_2	rate constant of propene dimerization reaction (B)	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
k_{b2}	reverse reaction (B) rate constant	s^{-1}
k_{b1}, k_{b3}	component desorption rate constants	s^{-1}

K_A, K_B, K_C	equilibrium constants of the reactions (A), (B), (C), respectively	$\text{dm}^3 \text{mol}^{-1}$
M_1, M_2	molar mass of propene and of its dimer, resp.	kg kmol^{-1}
n_s	maximum concentration of adsorption sites	mol g^{-1}
[P]	propene concentration in a gas phase	mol dm^{-3}
[P ₂]	propene dimer concentration in a gas phase	mol dm^{-3}
[PS] _s	sorbed propene monomer concentration	mol g^{-1}
[P ₂ S] _s	sorbed propene dimer concentration	mol g^{-1}
q	total specific amount of substance of propene adsorbed	mol g^{-1}
[S] _s	concentration of free adsorption sites	mol g^{-1}
t	time	s
T	thermodynamic temperature	K
θ	Celsius temperature	°C

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