

Model of activation of the cobalt foil as a catalyst for CO₂ methanation

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Abstract

A model related to variation in the concentration of active centers is proposed. Previously obtained experimental results are briefly reviewed together with presentation of complementary results. The results are generalized in the assumptions of the model. Two steps of activation of the Co foil are distinguished: (1) formation of potential centers as referred to surface development during redox pretreatment, (2) transformation of potential centers into active centers via autocatalytic reduction by hydrogen contained in the methanation mixture. A good fit to the kinetic results and agreement with available experimental facts verify the validity of the model. © 1997 Published by Elsevier Science B.V.

Keywords: Activation model; Cobalt catalyst; CO₂ methanation

1. Introduction

Heterogeneous catalysts require pretreatment in order to be transformed from a nearly inert state to an active one, thus meaning that the catalyst precursors have to be activated. However, they lose such an activity during their work in a catalytic reactor, that is to say, the catalysts undergo deactivation with time-on-stream (TOS). Hence, the active state is a specific, and unstable, state of a material called catalyst.

Changes in catalyst activity can be formally described by a commonly used performance

equation [1] but without any further insight into the nature of activation and deactivation processes.

Another possible way of investigating the problem consists in considering variable numbers of active centers in a given catalytic system [2]. The catalytic reaction proceeds only on the specific sites of the catalyst surface — called active centers. As soon as the population of these centers changes, the reaction rate also changes, provided that the turn-over frequency (TOF) on an active center is a specific constant value. Hence, observed continuous variation in the reaction rate (in stationary systems) can be interpreted as the variation of the number of active centers.

Alternatively, it could be assumed that the

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number of active centers is constant [3], and all changes in the rate of catalytic reaction are due to the changes in TOF. However, such a model, explaining continuous changes in the catalytic reaction rate, based on continuous changes in TOF, has not yet been applied.

The present paper intends (i) to propose a model of activation (based on a variable number of active centers and a constant TOF) in a definite catalytic system, and (ii) to verify assumptions in the model by appropriate kinetic and complementary experiments.

Methanation of CO_2 on the preoxidized cobalt foils has been chosen as a convenient model system.

The model consideration presented in this paper is a contribution to the study on the activation and deactivation of cobalt foil in CO_2 methanation, done in close cooperation with Prof. G. Wedler et al. from the University of Erlangen. Since deactivation has been found to be not a single process but comprised of several processes combined together, model consideration on deactivation requires justification based on experimental results distinguishing various reasons for the deactivation. The detailed description will be presented in a separate paper [4].

2. Experimental characterization of the activation processes

It has been known from studies by Amariglio et al. [5–8] that the initial activity (just after preoxidation) during methanation of CO_2 is about thousand times higher than the activity of an untreated foil. Amariglio et al., however, did not propose any consistent model of the cobalt foil activation, though he suggested that oxygen atoms promote its methanation activity in some unrecognized way. This inspired us to investigate the problem further and was a starting point to formulate first hypothetical models of activation.

The initial approach to modelling enabled us

to put several questions necessary to complete a set of consistent assumptions of the model. Consequently, to achieve this, a new characterization of the catalytic system has been performed in cooperation with Prof. G. Wedler. The most essential results of this study, which contribute to the experimental basis of the model, were included in the previous paper in series [9]. They, and some others, will be reviewed briefly, and then, the new and relevant facts will be introduced along with a short description of the experimental set-up and procedure.

2.1. Review of known facts

The tremendous increase in methanation activity after preoxidation of Co foils was confirmed [10], and moreover, additional sigmoidal increase in the activity was observed by us in thorough measurements of kinetics of CO_2 hydrogenation [11] — especially those done in a short TOS range [9,12]. The methanation activity was observed to be enhanced by either increasing the partial pressure of oxygen during preoxidation or by increasing the oxidation temperature.

The knowledge of the nature of cobalt activation has been enriched by characterization of both cobalt monocrystals [13–16] and polycrystalline cobalt [9,16,17]. It has been found that the reduction is limited only to the surface layers [9,17], unlike oxidation which can reach far, deep layers in the cobalt bulk [9,15,17,18]. This was evidenced by depth profiling with Auger electron spectroscopy and electron microscopy [9,18], and, additionally, by the temperature-programmed reduction and oxidation experiments [9,17]. Furthermore, repetition of redox cycles, applied as a pretreatment of the cobalt foil, causes an increase in the number of labile oxygen atoms (removable in the subsequent reduction step) up to the saturation value, observed after about 10 redox cycles [9,17]. A complementary increase of the maximum catalytic activity has been observed, up to a very

reproducible value [9,12]. This maximum activity is about 10^4 times higher than the activity of a well-reduced cobalt foil.

2.2. New facts

2.2.1. Experimental

The apparatus used in kinetic studies allows to carry out experiments in continuous flow of reactants. It comprises a gas supplying system, reactor and gas analyzing system. The gas supplying system consists of a hydrogen generator (Packard), flasks with N_2 — technical with 3200 ppm of O_2 (POCh), standard CO_2 and He (POCh), gas purifiers (Supelco), electronic flow controllers (ERG-100), and four- or six-port valves (Supelco). Characterization of the reactor type by the residence-time distribution of a tracer (CH_4 in He flow) allowed to classify it as a plug-flow reactor [12,19]. The reactor is equipped with a programmable heating device: oven, thermocouples and temperature programmer (Chinotherm 10A). The gas analyzing system is built of two alternatively working detectors (Chrom-5) fixed directly to the reactor outlet:

- a flame ionization detector applied during hydrogenation of CO_2 for continuous measurement of methane in the reactor outlet (the contribution of higher hydrocarbons in products of CO_2 hydrogenation was always less than 1%);
- a thermal conductivity detector applied in temperature-programmed reduction and oxidation.

The sample of catalyst used in all types of experiments presented in this paper, was a cobalt foil (Goodfellow, 99,9%, 0.05 mm thick, about 1.1 cm^2 of total geometrical area cut into 8 pieces). Prior the routine catalytical tests the initial sample of the foil was pretreated by a series of 10 redox cycles in order to obtain a reproducible activity in the methanation of CO_2 . The parameters of reduction and oxidation were the same as during the standard pretreatment (see below).

The procedure of all isothermic kinetic tests consisted of the following steps:

- the redox pretreatment: prereluction in H_2 30 ml/min for 1 h at 873 K, and preoxidation in N_2 containing 3200 ppm O_2 , 30 ml/min for 30 min at 873 K;
- catalytical CO_2 methanation performed at 573 K (also 473, 523, 623 K), in $H_2:CO_2 = 4:1$ with a flow rate 50 ml/min.

The experiments were carried out at atmospheric pressure. The values of flow rates refer to 101300 Pa and 293 K.

The described conditions of CO_2 methanation will be called *the standard conditions* of the methanation or simply *the standard methanation* in the whole paper (unless specified differently).

Temperature-programmed reduction (TPRed) was carried out in H_2 (flow rate 50 ml/min with a rate of temperature increase of 10 K/min) on the catalyst oxidized at the same conditions as those given above.

The preliminary characterization of the microreactor by the tracer time distribution provided determination of the response time, i.e. the period between the switching on the valve and getting the detector response, amounting 30 s for a total flow $F = 50\text{ ml/min}$. This was taken into account in establishing the 'zero time' for kinetic curves obtained during catalytic tests.

2.2.2. Results

After presentation of the known facts, the last question to be considered is: What process is responsible for increasing the activity of the catalyst in the initial period of CO_2 methanation? In order to answer it, the foil was tested by the catalytical reaction at its two different redox states. Curve *a* in Fig. 1 represents the typical result of the standard methanation at 573 K, i.e. when the catalyst at the oxidized state was exposed to the reaction mixture. In contrast, curve *b* corresponds to the analogous experiment in which the catalyst after usual preoxidation was reduced in H_2/He (4:1, 50 ml/min) at 573 K for 15 min, prior the standard methana-

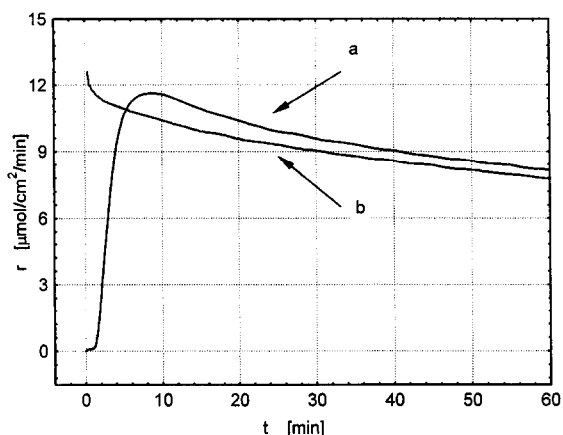


Fig. 1. Kinetic curves of methanation of CO_2 obtained at 573 K, in $\text{H}_2:\text{CO}_2 = 4:1$ with flow rate 50 ml/min. (a) Pretreating stopped at the oxidized state of Co foil, (b) pretreating stopped at the reduced state of Co foil.

tion. Since in this case the initial sigmoidal growth of the activity does not appear, it is obvious that the catalyst in the reduced state of the surface is active, and reduction is the reason for the growth in activity.

The total amount of water which can be evaluated during reduction, estimated from TPRed (e.g. Fig. 2), and being the measure of reducible cobalt cations, amounts to $41 \mu\text{mol}/\text{cm}^2$.

Kinetics of the activation depends on temperature. The lower the reaction temperature, the longer is the period of activation and the lower

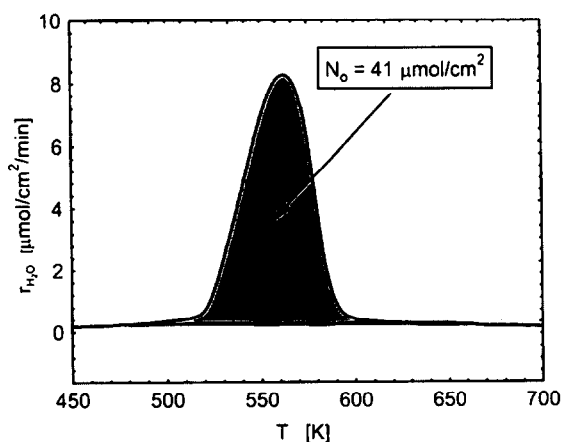


Fig. 2. Temperature-programmed reduction (TPRed) of Co foil performed in H_2 , 50 ml/min, with a heating rate of 10 K/min.

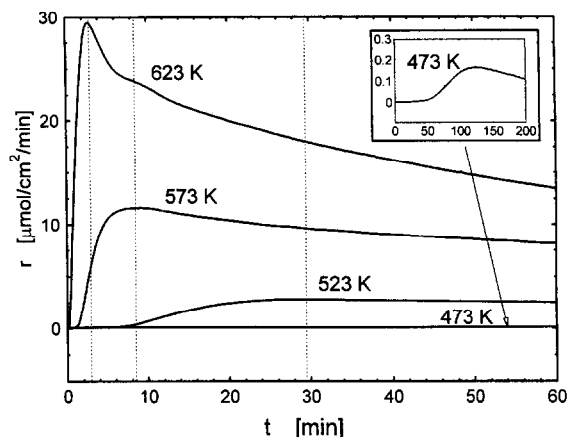


Fig. 3. Kinetic curves of methanation of CO_2 obtained at different temperatures, in $\text{H}_2:\text{CO}_2 = 4:1$, 50 ml/min.

maximum activity. For instance, at 473 K, it lasted about 2 h but the activity was at the lowest limit of the detector sensitivity, and, at 623 K, it lasted only 3 min. The set of kinetic curves obtained at various temperatures is presented in Fig. 3. The inset in Fig. 3 shows the experiment carried out at 473 K in enlarged coordinates.

3. Model presentation

Two types of centers are distinguished:

1. Potential centers (\otimes), defined as cobalt cations in the surface layers, which can be reduced by hydrogen at the standard conditions.
2. Active centers ($*$), defined as clusters of cobalt atoms, formed on the catalyst surface from the reduced cobalt cations.

A sequence of the reduction and oxidation pretreatment (the redox cycles) causes a step-by-step increase in the number of potential centers. It can be explained as follows. Oxidation of a metal domain in the fresh cobalt foil results in formation of many oxide nuclei which grow into oxide subgrains. These subgrains are reduced superficially in the next reduction step. Apparently, the following oxidation step has to form even smaller oxide subgrains, and so on.

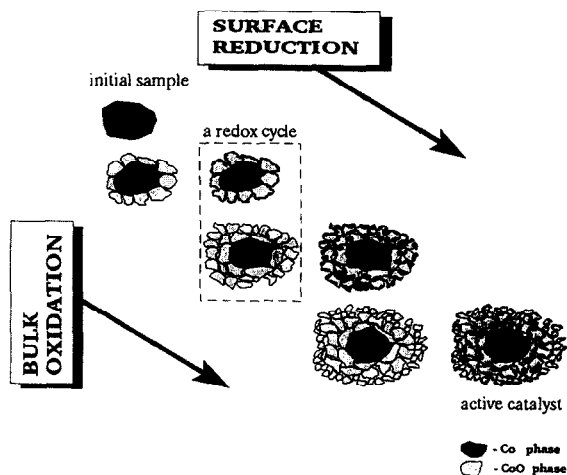


Fig. 4. Scheme of development of the surface of Co foil in subsequent redox cycles.

Thus, the initial cobalt grain is divided into many smaller sub-subgrains which are bound loosely in the total grain. Such a material has a larger specific surface and a high cobalt dispersion (Fig. 4) manifested in SEM micrographs [9].

Preliminary activation of cobalt in the redox cycles leads to the development of its surface, and, as a consequence, to an increase in the number of the potential centers. The concentration of these centers depends on 4 parameters: temperature of oxidation, pressure of oxygen, times of oxidation and reduction, and number of redox cycles. Usually, after 10 cycles at the standard conditions of the reaction, the number of potential centers on the surface of so prepared catalyst reaches the maximum value, N_0 .

Admission of a hydrogen-containing reaction mixture into the reactor causes *proper activation*, i.e. transformation of the potential (\otimes) centers into active ($*$) ones. It is the reason for increase of the methanation rate during the first minutes of the catalytic methanation (curve a in Fig. 1).

Reduction of the totally oxidized catalyst by molecular hydrogen must be a very slow reaction determined by the rate constant k_{1a} of formation of a water precursor (see the scheme in Fig. 5). However, appearance of reduced

cobalt atoms enables fast dissociative adsorption of hydrogen molecules characterized by an equilibrium constant, K_{H_2} . There is experimental evidence, e.g. [20,21], that H_2 is dissociatively chemisorbed on cobalt films or monocrystals. Surface species, H^* , react easily with surface oxide forming water precursors with a rate constant k_{1c} . Hence, the transformation of the potential centers into active ones can be described by the formalism of the autocatalytic reaction. This implies that there are two types of reduction of the surface cobalt oxide: (1) reduction by molecular hydrogen (*non-catalyzed*), (2) reduction by atomic surface hydrogen (*catalyzed*). Formation of water precursors (r_{1a}) must be a rate determining step of the non-catalyzed reduction (RDS act). This is simply a precondition for the proper activation.

Moreover, the commonly approved model of CO_2 methanation, proposed by [22–24], has been included in the model consideration. It is based on dissociation of CO_2 , and formation of carbon species which are subsequently hydrogenated to methane precursors, arbitrarily denoted by CH_2^* in Fig. 5. At the standard conditions of the reaction, hydrogenation of methane precursors is a rate determining step for the overall reaction. For the sake of convenience, hydrogenation of CH_2^* has been chosen as a representative rate determining step (RDS met) in further calculations.

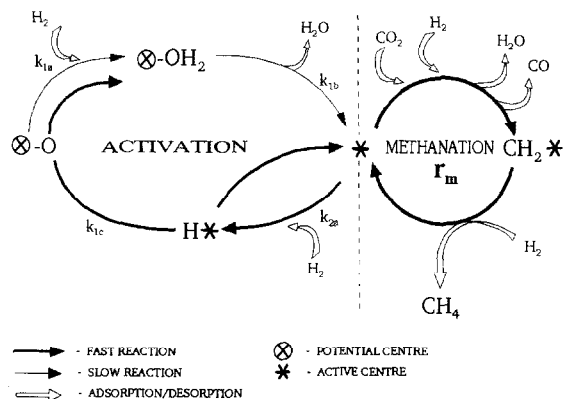


Fig. 5. Mechanism of activation based on the autocatalytical reduction of potential centers.

In accordance with our experimental data, the overall rate constant for the methanation (k_m) is much higher than the overall rate constant for activation (k_{act}). If it were opposite, we would have observed an initial increase of the methanation rate also in Fig. 1b, where the catalyst was reduced just before admission of the reaction mixture. No such a behavior was noticed, which means that the quasi-steady state of the methanation is reached much faster than it can be measured (in our case the data collecting frequency was 0.5 s^{-1}). In other words, while the population of active centers grows, methanation runs through the continuity of its steady states. Different widths of arrows, in Fig. 5, correspond to the differences in specific rates of the partial reactions.

It should be added that the model of catalyst activation is limited to the period of time-on-stream up to the maximum concentration of active centers (N_{max}), $0 < \text{TOS} < t_{max}$, and temperature below 630 K. At these conditions, the rate of catalyst deactivation (r_{dea}) is negligible in comparison with both rates of methanation (r_m) and activation (r_{act}).

4. Model formalism

4.1. Limits and definitions

$t = \text{TOS}$	$0 < t < t_{max}$	period of catalyst activation
$k_m \gg k_{act}$	and $r_{dea} \cong 0$	relations between rates of methanation, activation and deactivation
$T_m = \text{const}$	$[\text{H}_2], [\text{CO}_2] = \text{const}$	isothermic methanation concentration of substrates in the differential reactor

The specific rates of methanation and activation are related to the geometric area of the initial sample of the Co foil (without any pre-treatment). The rate changes due to the change

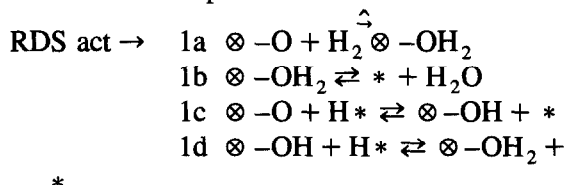
in concentration of the active centers, *, related to 1 cm^2 of the initial sample:

$$r_m = \frac{1}{S} \frac{dn_{\text{CH}_4}}{dt}$$

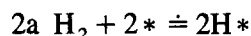
$$r_{act} = \frac{d[*]}{dt} \left[\frac{\mu\text{mol}}{\text{cm}^2 \text{min}} \right] \quad (1)$$

4.2. Chemical equations

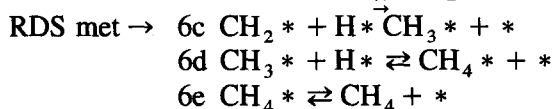
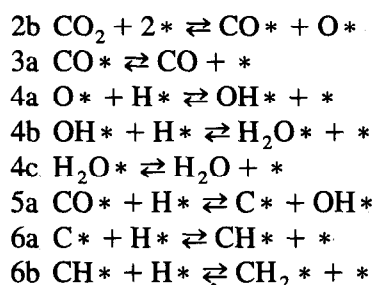
Reduction of potential centers:



Fast dissociative adsorption:



Mechanism of methanation of CO_2 :



Notation: \rightleftharpoons , reversible reaction; $\xrightarrow{\hat{}}$, rate determining step (RDS); \rightleftharpoons , fast reached equilibrium.

4.3. Model functions

They are derived in two steps:

4.3.1. Concentration of active centers [*]

Solving a balance equation:

$$\begin{aligned} \frac{d[*]}{dt} &= -r_{1a} - r_{1c} \\ &= -k_{1a}[\text{H}_2][*] - k_{1c}[\text{H}^*][*] \quad (2) \end{aligned}$$

under the assumption

$$N_{\max} \approx [*] + [\otimes] + [H^*] \text{ and } k_m \gg k_{\text{act}} \quad (3)$$

$$[*] = \frac{N_{\max} k_{1a} \sqrt{[H_2]}}{\sqrt{K_{H_2}}} \times \frac{1 - e^{-(k_{1a}[H_2] + k_{1c} N_{\max})t}}{k_{1a}[H_2] + k_{1c} N_{\max} e^{-(k_{1a}[H_2] + k_{1c} N_{\max})t}} \quad (4)$$

4.3.2. Overall rate of methanation r_m

At quasi-steady state:

$$2r_{2b} - r_{3a} = r_{6c} \quad (5)$$

$$r_m = k_{6c} [CH_2^*] [H^*] \cong 2k_{2b} [CO_2] [*]^2 \quad (6)$$

$$r_m = 2 \frac{k_{2b} [CO_2] [H_2]}{K_{H_2}} \times \left(N_{\max} k_{1a} \left\{ 1 - e^{-(k_{1a}[H_2] + k_{1c} N_{\max})t} \right\} / \left\{ k_{1a}[H_2] + k_{1c} N_{\max} e^{-(k_{1a}[H_2] + k_{1c} N_{\max})t} \right\} \right)^2 \quad (7)$$

5. Model verification and discussion

Nonlinear regression was used so as to fit the model function (Eq. (7)) to the experimental data. The parameters were optimized with the use of the quasi-Newton method or, if it was necessary, the Simplex method available in the commercial package CSS:STATISTICA.

The set of data available for verification comprises 8 kinetic curves obtained at different temperatures. The slowest measurable rate of CO_2 methanation determined the lowest temperature for the verification, i.e. 473 K. The upper temperature limit is 623 K. At this temperature, the period of proper activation lasts less than 3 min. As the time of proper activation (t_{\max}) prolongs with temperature, and the density of points is constant (0.5 s^{-1}), so the number of points belonging to kinetic curves

decreases from about 3000 (473 K) to 100 (623 K).

The examples of verification tests are presented in Fig. 6 a–d. The results of the function fitting (—) to the experimental data (···) are very good. The standard deviation related to the values of the predicted function stays at about 1%, except for 623 K at which it is equal to 3%. The correlation coefficient decreases with temperature from, on average, 0.9998 at 473 K to 0.9995 at 623 K. The highest deviation between experimental data and the predicted function occurs in the beginning of activation at 623 K (see Fig. 6d). The lowest sensitivity of the FID was used at this temperature, due to the relatively high signal of methane at the maximum. For this reason, small initial values of the rate of methane formation have the largest experimental error (as well as the lowest number of points), thus influencing the quality of fitting at higher temperature.

The parameter optimization provided determination of four parameters of the model presented in Fig. 7:

- the maximum number of active centers, N_{\max} ;
- the rate constants of non-catalyzed, k_{1a} , and catalyzed, k_{1c} , reduction of potential centers;
- the inseparable parameter P , the ratio of the rate constant of adsorption of CO_2 on active centers, k_{2b} , to the equilibrium constant of dissociative adsorption of H_2 , K_{H_2} .

The first adjustable parameter, N_{\max} , increases with the temperature of methanation from about $6 \mu\text{mol}/\text{cm}^2$ at 473 K to $39 \mu\text{mol}/\text{cm}^2$ at 623 K. The value of N_{\max} for 623 K is almost equal to the number of reducible cobalt atoms, $N_0(\text{TPRed})$ obtained from TPRed (see Fig. 2). Apparently, at lower temperature, activation does not lead to complete reduction of the surface Co cations (during TPRed surface reduction completed at about 620 K).

In order to determine the extent of activation due to redox cycles we can compare the concentration of active centers at both initial and reproducible states of Co foil. The concentration of Co atoms on the densest [0001] plane of Co

monocrystal (hcp) related to geometric area will serve as a reference value and a model value of the number of active centers on the ideal cobalt foil. This value amounting to $4.1 \cdot 10^{-3} \mu\text{mol}/\text{cm}^2$, is four orders of magnitude smaller than the one of the active foil ($N_0(\text{TPRed})$ and N_{max}).

The rate constants of non-catalyzed reduction (k_{1a}) and catalyzed reduction (k_{1c}) increase with temperature. The certainty of optimization of both parameters lowers with temperature because divergences between the values of parameters at a given temperature (see Fig. 7) as well as the standard deviations (from optimization) grow with temperature (especially for k_{1c}). It seems to be quite plausible that the boundary temperature for the assumption of negligible deactivation is located around 623 K.

According to our expectations, as can be independently deduced from the model, the rate constant k_{1a} is less than k_{1c} within the whole

range of the used reaction temperatures. Let us compare the rates calculated from both constants (Eq. (2)) with the number of collisions of H_2 molecules estimated from the theory of the ideal gas (C_n). The maximum rates of non-catalyzed ($r_{1a}(t_{\text{max}})$) and catalyzed ($r_{1c}(t_{\text{max}})$) reductions are 8 orders of magnitude lower than C_n . The discussed values and the formulas are given in Table 1. At last, comparison of the activation energies of the non-catalyzed and catalyzed reductions — their estimated values amounting to 106 ± 4 and 28 ± 2 kJ/mol, respectively — gives also a reasonable result. The fit of the Arrhenius equation to both parameters is shown as a solid line in Fig. 7 (correlation coefficients for $k_{1c} = 0.97$, for $k_{1a} = 0.998$).

The last optimized parameter, P , can be treated as a competition factor between chemisorption of CO_2 and H_2 on the same adsorption centers. It grows with temperature. The dependence of P on temperature fulfills the

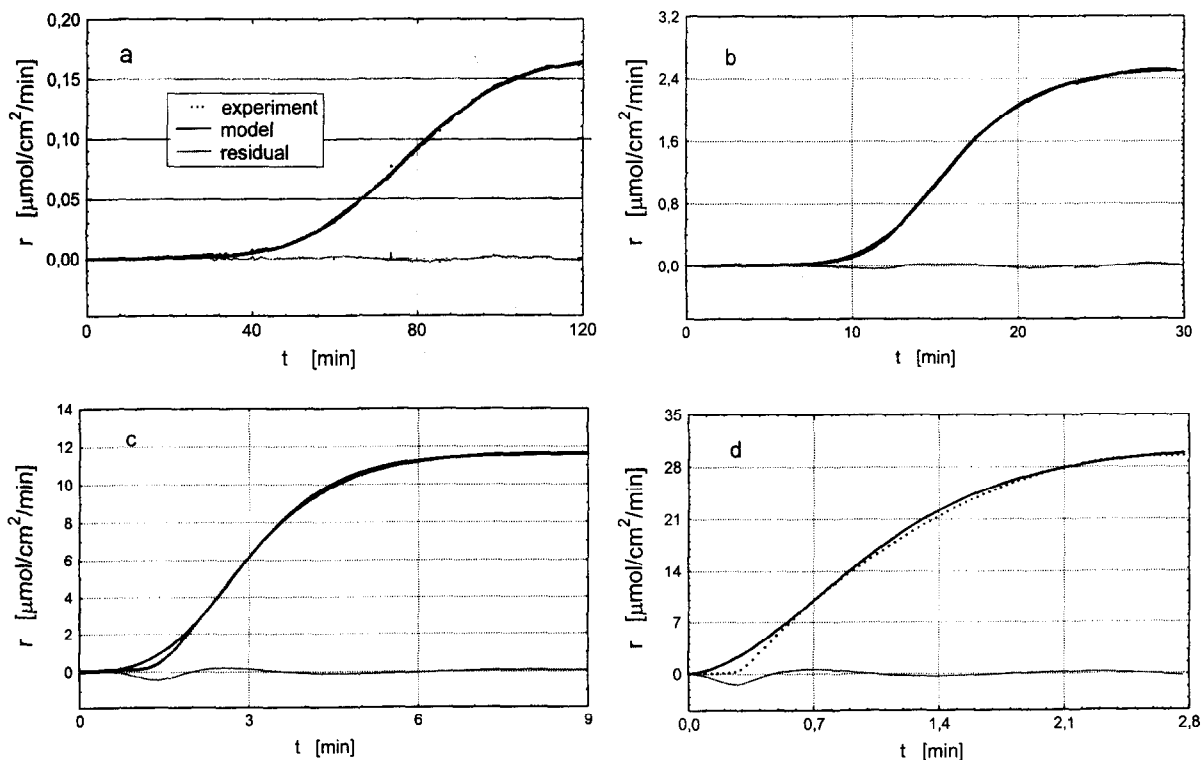


Fig. 6. Model function fitting to the kinetic curves obtained at $\text{H}_2:\text{CO}_2 = 4:1$, 50 ml/min: (—) model function fitting, (···) experimental data, (---) residuals, difference between predicted and experimental values: (a) 473 K, (b) 523 K, (c) 573 K (d) 623 K.

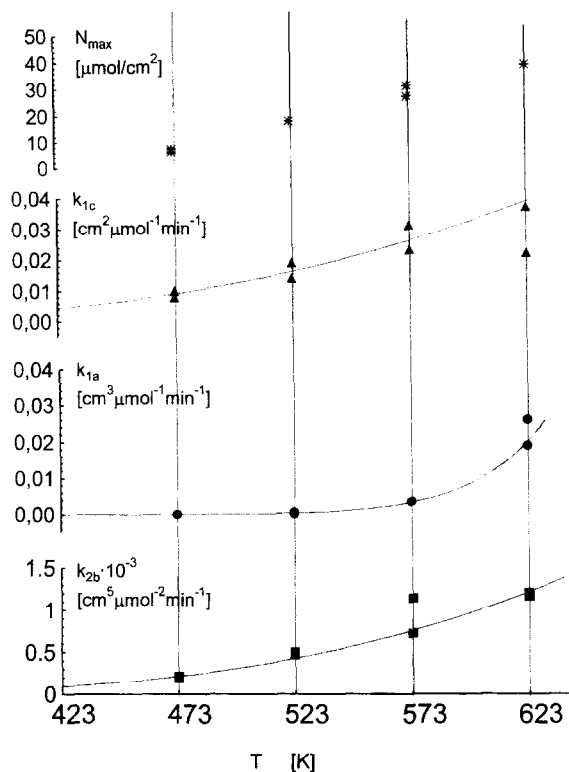


Fig. 7. Parameters of the model of activation obtained at different reaction temperatures: N_{\max} – maximum number of active centers, k_{1c} – rate constants of the catalyzed reduction of potential centers, k_{1a} – rate constants of the non-catalyzed reduction of potential centers, P – inseparable parameter which is the ratio between the rate constant of dissociative adsorption of CO_2 (k_{2b}) and equilibrium constant of dissociative adsorption of H_2 (K_{H_2}); (—) fitting of the Arrhenius equation.

Arrhenius equation. Formally treated, the apparent energy for this parameter equals 22 kJ/mol (correlation coefficient 0.97).

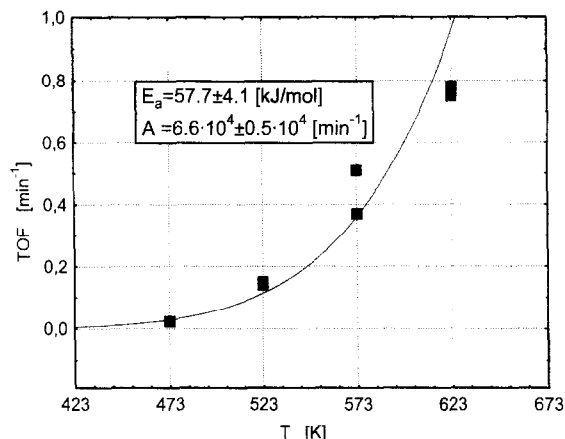


Fig. 8. Turn-over frequency (TOF) of methanation (■); fitting of Arrhenius equation (—).

The model of activation allows to calculate TOF of methanation from the maximum rate of methanation ($r_m(t_{\max})$) based on values of N_{\max} estimated from the model. The results are presented in Fig. 8 along with the values of the activation energy (E_a) and the preexponential factor (A). The values of TOF and A can be compared with the summary frequency of collisions of H_2 and CO_2 with an active center (C_f). The values of C_f were estimated from the ideal gas theory including the stoichiometry of methanation. They are presented in Table 2.

The preexponential factor A is 2 orders of magnitude lower than the summary frequency C_f , which appears to be quite convincing. Certainly, TOF is around 7 orders of magnitude lower than C_f . The ratio of TOF to the summary

Table 1

Comparison of the number of collisions of H_2 molecules and the maximum rates of the non-catalyzed reduction (r_{1a}) and catalyzed reduction (r_{1c}) of Co surface oxide

T (K)	N_{\max} ($\mu\text{mol}/\text{cm}^2$)	r_{1a} ($\mu\text{mol}/\text{cm}^2 \text{min}$)	r_{1c} ($\mu\text{mol}/\text{cm}^2 \text{min}$)	$C_n(\text{H}_2)$ ($\mu\text{mol}/\text{cm}^2 \text{min}$)
473	6.4	0.036	2.2	$1.12 \cdot 10^8$
473	7.2	0.040	1.9	$1.12 \cdot 10^8$
523	18	0.085	7.9	$1.18 \cdot 10^8$
523	28	0.41	5.8	$1.18 \cdot 10^8$
573	26	1.2	9.6	$1.23 \cdot 10^8$
573	31	1.6	8.7	$1.23 \cdot 10^8$
623	39	1.7	1.7	$1.28 \cdot 10^8$
623	39	1.3	2.9	$1.28 \cdot 10^8$

$$r_{1a} = k_{1a}[\text{H}_2](N_0(\text{TPRed}) - N_{\max})$$

$$r_{1c} = k_{1c} N_{\max}(N_0(\text{TPRed}) - N_{\max})$$

Table 2

Comparison of the summary frequency of collisions of H₂ and CO₂ molecules, C_f, and TOF of methanation

T (K)	N _{max} (μmol/cm ²)	TOF (min ⁻¹)	C _f (min ⁻¹)	C _f · e ^{-E_a/RT} (min ⁻¹)	s
473	6.4	0.023	5.3 · 10 ⁶	2.23	0.010
473	7.2	0.023	4.6 · 10 ⁶	1.95	0.012
523	18	0.15	1.9 · 10 ⁶	3.39	0.044
523	18	0.14	1.9 · 10 ⁶	3.39	0.041
573	26	0.37	1.2 · 10 ⁶	6.56	0.056
573	31	0.51	1.4 · 10 ⁶	7.53	0.068
623	39	0.75	1.0 · 10 ⁶	14.38	0.052
623	39	0.78	1.0 · 10 ⁶	14.38	0.054

$$C_f = \frac{1}{4} \frac{C_n(\text{H}_2)}{N_{\text{max}}} + \frac{C_n(\text{CO}_2)}{N_{\text{max}}}$$

$$s = \frac{\text{TOF}}{C_f \exp(-E_a/RT)}$$

frequency of active collisions (for the formula see Table 2) characterizes a kind of a steric factor for methanation of CO₂ (*s*). After initial increase with temperature, *s* seems to stabilize at around 0.06.

As mentioned before, the model is limited to the cases when deactivation of the catalyst is negligible. This assumption is fulfilled within the period of continuous increase of the catalytic activity. However, the influence of deactivation on the methanation rate grows in the vicinity of the maximum activity. Although, as observed in TPR [4,9], sintering was noticeable at temperatures higher than 630 K; it could interfere with activation at 623 K, which in turn could influence the values of the model parameters at this temperature.

The problems concerning the catalyst deactivation have been described in the previous paper [9]. Complementary results and a model of deactivation will be presented in the next paper [4].

6. List of symbols

⊗ potential centers, cobalt cations in surface layers of Co foil

* active centers, cobalt clusters
 A preexponential factor in the Arrhenius equation
 C_n number of collisions [μmol/cm²/min]
 C_f frequency of collisions with an active center [min⁻¹]
 [CO₂] concentration of CO₂ in the gas phase [μmol/cm³]
 [H₂] concentration of H₂ in the gas phase [μmol/cm³]
 E_a activation energy [kJ/mol]
k rate constant
k overall rate constant
 K_{H₂} equilibrium constant of H₂ dissociative adsorption
 N₀ maximum number of potential centers on Co foil obtained after more than 10 redox cycles at the standard conditions, maximum available number of active centers.
 N_{max} maximum number of active centers on Co foil at a given reaction temperature (at *t*_{max}) [μmol/cm²]
 P inseparable parameter of the activation model *k*_{2b}/K_{H₂}
r rate [μmol/cm²/min]
r overall rate [μmol/cm²/min]
 RDS rate determining step

S	geometrical area of a clean untreated initial sample of Co foil [cm^2]
s	steric factor
t	time-on-stream [min]
t_{max}	time-on-stream at the maximum of activity of Co foil during methanation of CO_2
T	temperature [K]
Lower indexes	
1a	non-catalyzed reduction of \otimes
1c	catalyzed reduction of \otimes
2a	dissociative adsorption of H_2
2b	dissociative adsorption of CO_2
3a	desorption of CO in RWGS
6c	rate determining step in methanation of CO_2
act	activation
dea	deactivation
m	methanation

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