KINETICS OF THE CARBON MONOXIDE CONVERSION WITH STEAM AT ELEVATED PRESSURES

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The kinetics of the carbon monoxide conversion with steam on a Czechoslovak FeCr catalyst was investigated. The experimental data were obtained on a gradient-free differential reactor with recirculating gaseous phase at temperatures of 633 and 693 K and pressures from the range 0·1 – 0·9 MPa. The evaluation of experimental data showed that the reaction rate increases with increasing pressure according to a downward convex curve and that it also increases with increasing content of carbon monoxide in the gas and with decreasing content of carbon dioxide. The reaction kinetics was described by an equation derived from the Langmuir–Hinshelwood concept for the case when the limiting step of the reaction is a surface reaction.

The kinetics of the conversion of carbon monoxide with steam on FeCr catalyst has been studied for several ten years. During the last 40 years, more than 20 different kinetic equations were proposed. Differences among the authors appear especially in their opinions of the reaction mechanism and the effect of pressure on the reaction rate. Reasons for this can be related to limited possibilities of the most often employed integral method[1-8] as well as to the fact that the kinetic measurements were mostly performed at atmospheric pressure only[1-6]. More exact differential methods[9-12] have become widely used only recently.

It was the aim of our work to obtain reliable experimental data on a Czechoslovak medium temperature catalyst and to interpret them by a kinetic equation which would express correctly the effect of pressure on the reaction rate. To that purpose we employed an apparatus with a differential reactor and recirculation of the gaseous mixture, which enabled to perform the measurements also at elevated pressures.

EXPERIMENTAL

Necessary kinetic measurements were performed in an apparatus whose main parts, *i.e.*, the reactor, recirculation loop and gas pump, were made of an AKVS stainless steel. The input line for the gas, which included purifying columns and connecting piping, was made of brass or copper capillaries resp. The apparatus is illustrated in Fig. 1.

Carbon monoxide employed for the measurement was fed from the pressure cylinder to a reduction valve, passed through purifying columns, in the mixing vessel it mixed with steam and finally the mixture entered the recirculation loop. The necessary amount of water was added into the heated mixing vessel by a piston micropump. During the measurements at atmospheric pressure, inlet tubes with N_2 and H_2 were also connected to the apparatus, so that the effect of reaction components on the reaction course could be investigated. Rates of flow of the gases were controled by regulators and determined by capillary flow meters.

The recirculation loop, which included the reactor, pump and connecting piping, was heated by a resistance heating above the dew point. The reactor consisted of an outer jacket with a lid and an inner tube containing the catalyst deposited on a stainless gauze. The reaction mixture entered the space between the jacket with the lid and the inner tube, where it was preheated to a temperature close to the reaction one, and then it was fed to the tube with the catalyst. The temperature was measured with a Fe–constantan thermocouple inside a probe reaching to the catalyst bed. The pump was of the magnetic type[13] with a maximum output of 800 l/h. The gaseous mixture leaving the recirculation loop was fed to a pin valve and then to a water condenser for desiccation. The amount of the dry mixture was determined by a wet gasometer. Data on the CO and CO_2 contents were obtained on the Orsat device.

The measurements were performed with $0.4-0.63$ mm — large grains of the Czechoslovak Cherox 31—01 catalyst, which were obtained by crushing of pellets of industrial size. The catalyst was reduced with a $1:2$ mixture of CO and steam.

The data on the composition of the gaseous mixture, the rate of flow and the total pressure in the reactor were used for calculating the partial pressures of single components and the reaction rate. Carbon monoxide was selected as the key component. For the case, when the original mixture did not contain CO_2, the following relations were employed for the calculation

$$r = F_{CO}^0 x / W \qquad (1)$$
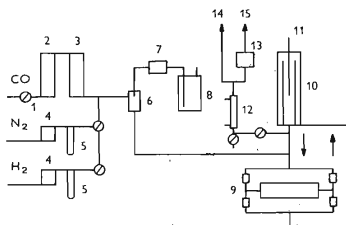
$$x = N_{CO_2}/(N_{CO_2} + N_{CO}) \qquad (2)$$

$$p_{CO} = N_{CO}^0 (1 - x) P \qquad (3)$$

$$p_{H_2O} = \left(N_{H_2O}^0 - N_{CO}^{0'} x\right) P \qquad (4)$$

Fig. 1

The Scheme of the Apparatus

1 Reduction valve, 2 column with active carbon, 3 column with a Cu catalyst, 4 pressure regulator, 5 capillary flow meter, 6 mixer, 7 dosing micropump, 8 water reservoir, 9 magnetic pump, 10 reactor, 11 thermocouple, 12 water condenser, 13 wet gasometer, 14 sampling of gases for the analysis, 15 exhaust.

$$p_{CO_2} = N_{CO}^0 xP \qquad (5)$$

$$p_{H_2} = N_{H_2}^0 + N_{CO}^0 xP , \qquad (6)$$

where r is the reaction rate, W catalyst mass, F_{CO}^0 CO feed, x degree of conversion, p_i partial pressure of component i, P total pressure in the reactor, N_i mole fraction of component i in the dry gas at the reactor outlet, N_i^0 mole fraction of component i in wet feed.

Experimental data were determined at conditions corresponding to the kinetic region at temperatures of 633 and 693 K. These data were divided into two sets. The first set was obtained in the pressure range 0·1—0·3 MPa and contained 56 points at 633 K and 57 points at 693 K. The composition of the reaction mixture oscillated in the ranges CO 3—4, H_2O 10—70, CO_2 1—30 and H_2 1—70 vol.%. These data were employed for the selection of the kinetic equation and for the evaluation of its constants. The second set comprised data obtained with the gas containing CO and H_2O only at the H_2O/CO ratio of 1—4 and at pressures of 0·5 and 0·9 MPa. This set, which contained 20 points on the whole, was used for the verification of the kinetic equation at elevated pressures.

RESULTS AND DISCUSSION

The evaluation of our experimental data revealed several relations, which enabled a preliminary selection of kinetic equations. To this purpose we constructed curves illustrating the effect of the composition of the gaseous mixture and the total pressure on the reaction rate (Figs 2—4). According to mutual positions of curves in Fig. 2, the reaction rate increases considerably in the presence of CO. On the other hand — as it is obvious from Fig. 3 — the effect of H_2O is less pronounced. At higher degrees of conversion, the reaction rate mildly increases in the presence of steam (besides other things, also due to its favourable effect on the equilibrium composition), at lower concentrations the curves cross each other. The replacement of N_2 in the gaseous mixture with hydrogen exhibits almost no effect on the reaction course.
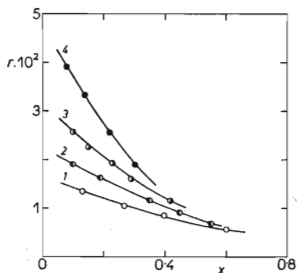

Fig. 2

The Effect of CO on the Reaction Rate r (mol/kg s) at 633 K and Constant $p_{H_2O}^0 = 0.05$ MPa

p_{CO}^0: 1 0·01, 2 0·0167, 3 0·025, 4 0·05 MPa.

Of the products, CO_2 possesses a considerable retarding effect on the reaction, which has already been proved for this catalyst in works by Dong[12] and Riša[14]. The effect of pressure is illustrated in Fig. 4. It is the main criterion, which enables to estimate preliminarily the suitability of a given kinetic equation. It follows from a comparison of our experimental pressure dependence of the reaction rate with the dependences of single kinetic equations derived from the Langmuir–Hinshelwood concept, that only such mechanisms can be taken into account which yield a downward convex pressure dependence of the reaction rate. These mechanisms together with the corresponding equations are outlined below: CO and H_2O are adsorbed without dissociation, the limiting step is the surface reaction between the adsorbed molecules

$$r = \frac{k[p_{CO}p_{H_2O} - (p_{CO_2}p_{H_2}/K)]}{[1 + K_{CO}p_{CO} + K_{H_2O}p_{H_2O} + K_{CO_2}p_{CO_2}]^2} . \tag{7}$$

CO is adsorbed without dissociation, H_2O is adsorbed with dissociation, the limiting step is the surface reaction between the adsorbed particles

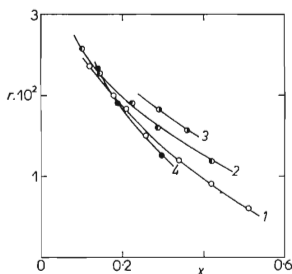$$r = \frac{k[p_{CO}p_{H_2O} - (p_{CO_2}p_{H_2}/K)]}{[1 + \sqrt{(K_{H_2O}p_{H_2O})} + K_{CO}p_{CO} + K_{CO_2}p_{CO_2} + K_{H_2}p_{H_2}]^3} . \tag{8}$$

FIG. 3

The Effect of H_2O on the Reaction Rate r (mol/kg s) at 633 K and Constant $p_{CO}^0 = 0.025$ MPa.
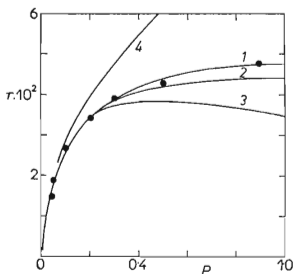
$p_{H_2O}^0$: 1 0.025, 2 0.05, 3 0.075, 4 0.025 MPa
$p_{H_2}^0 = 0.05$ MPa.

FIG. 4

The Dependence of the Reaction Rate r (mol/kg s) on Pressure p (MPa) at 633 K, the Ratio $H_2O/CO = 1$ and the Degree of Conversion $x = 0.2$

1 Experimental; Calculated by Eq.: 2 (7); 3 (8); 4 (15).

H_2O is adsorbed with dissociation, CO reacts with particles adsorbed from the gaseous phase, the limiting step is the surface reaction

$$r = \frac{k[p_{CO}p_{H_2O} - (p_{CO_2}p_{H_2}/K)]}{[1 + \sqrt{(K_{H_2O}p_{H_2H})} + K_{CO}p_{CH} + K_{CO_2}p_{CO_2} + K_{H_2}p_{H_2}]^2} . \qquad (9)$$

CO and H_2O are adsorbed without dissociation, the limiting step is the adsorption of CO

$$r = \frac{k[p_{CO} - (p_{CO_2}p_{H_2}/p_{H_2O}K)]}{1 + (K_{CO}p_{CO_2}p_{H_2}/p_{H_2O}K) + K_{H_2O}p_{H_2O} + K_{CO_2}p_{CO_2} + K_{H_2}p_{H_2}} . \qquad (10)$$

CO is adsorbed without dissociation, H_2O is adsorbed with dissociation, the limiting step is the adsorption of CO

$$r = \frac{k[p_{CO} - (p_{CO_2}p_{H_2}/p_{H_2 2O}K)]}{1 + (K_{CO}p_{CO_2}p_{H_2}/p_{H_2O}K) + \sqrt{(K_{H_2O}p_{H_2O})} + K_{CO_2}p_{CO_2} + K_{H_2}p_{H_2}} . \qquad (11)$$

An adequate pressure dependence of the reaction rate is offered also by two other mechanisms, in which both CO and H_2O are adsorbed (in one case with dissociation of H_2O) and the limiting step is the adsorption of H_2O. However, in both cases the kinetic equations indicate that the reaction rate is affected most significantly by steam, which contradicts experimental observations. Consequently, they can be excluded, too.

The form of equations derived on the basis of the Temkin two-step mechanism for the case of both a homogeneous and a heterogeneous catalyst surface leads to a linear dependence of the reaction rate on pressure. Therefore it cannot be expected that equations derived in this manner could interpret our experimental data with sufficient accuracy. Nevertheless, rather for illustration, two equations were selected for a quantitative evaluation of our data in the region of a high degree of saturation of the heterogeneous catalyst surface with oxygen[11]

$$r = k \frac{p_{CO}p_{H_2O} - (p_{CO_2}p_{H_2}/K)}{Ap_{H_2O} + p_{CO_2}} , \qquad (12)$$

and the second one for the reaction proceeding on the homogeneous catalyst surface[15]

$$r = \frac{\overrightarrow{k_1}\overrightarrow{k_2}p_{H_2O}p_{CO} - \overleftarrow{k_1}\overleftarrow{k_2}p_{CO_2}p_{H_2}}{\overrightarrow{k_1}p_{H_2O} + \overleftarrow{k_1}p_{H_2} + \overrightarrow{k_2}p_{CO} + \overleftarrow{k_2}p_{CO_2}} . \qquad (13)$$

TABLE I

Results of the Correlation of Experimental Data Obtained at Pressures of $0.1-0.3$ MPa by the Kinetic Equations

Eq.	T, K	k^a	K_{CO} MPa^{-1}	K_{H_2O} MPa^{-1}	K_{CO_2} MPa^{-1}	Deviation, %	
						mean	max.
(7)	633	283·0	21·6	41·7	56·7	8·5	24
	693	754·9	3·2	31·3	39·5	6·1	24
(8)	633	4 958·9	18·7	462·2	54·0	11·1	39
	693	9 514·9	3·0	256·0	35·3	7·7	32
(9)	633	115·0	−12·0	−198·8	−36·9	18·4	122
	693	577·1	0·5	−231·0	−35·3	9·8	41
(10)	633	1·2	−187·2	—	64·0	13·3	39
	693	5·4	63·1	—	36·3	7·1	32
(11)	633	1·2	−190·5	—	63·5	13·3	40
	693	5·0	47·0	−0·2	35·7	7·1	32
(12)	633	0·2	—	$A = 0.02$	—	58·9	213
	693	1·4	—	$A = 0.04$	—	43·7	170
(13)	633	—	0.1^b	1.5^c	2.9^d	36·1	64
	693	—	0·3	0·3	0·6	27·8	63
(15)	633	$2.2 . 10^{-2}$	—	—	—	12·3	35
	693	$12.9 . 10^{-2}$	—	—	—	7·7	37

^{a} The dimension of k depends on the form of the equation, the reaction rate is in mol/kg s; ^{b} $1/\vec{k_1}$; ^{c} $1/\vec{k_2}$; ^{d} $\vec{k_2}/\vec{k_1}\vec{k_2}$.

TABLE II

The Comparison of the Validity of Kinetic Equations (7), (8) and (15)

P, MPa	T, K	Deviation mean/maximum, %		
		(7)	(8)	(15)
0·5	633	8/15	18/30	19/37
0·9	633	14/16	31/44	43/61
0·5	693	9/17	18/31	30/54
0·9	693	13/26	25/36	48/73

Of empirical equations, the kinetic equation of the power-law type was being examined

$$r = kp_{CO}^a p_{H_2O}^b p_{CO_2}^c p_{H_2}^d [1 - (p_{CO_2}p_{H_2}/Kp_{CO}p_{H_2O})] . \qquad (14)$$

The evaluation of exponents in this equation yielded the following values: $a = 0.8$, $b = 0.05$, $c = -0.4$ at 633 K and $a = 1$, $b = 0.05$, $c = -0.6$ at 693 K. After the rounding-off of the exponents, the following equation — originally proposed by Atroshchenko[2] — was obtained

$$r = kp_{CO}p_{CO_2}^{-0.5}[1 - (p_{CO_2}p_{H_2}/Kp_{CO}p_{H_2O})] . \qquad (15)$$

The constants in the kinetic equations were calculated by the linear regression on a computer. In view of the fact that the rate of the forward reaction is not affected by hydrogen, we assumed that $K_{H_2} = 0$ and $d = 0$. We also assumed a negligible adsorption of inert N_2. The adequacy of a model was evaluated on the basis of the mean relative deviation between the experimental and calculated value of the reaction rate.

Results of our calculations are in Table I. Equations, in which at least one constant assumes negative values significantly different from zero, must be eliminated as inappropriate; this argument excludes Eqs (9)−(11) for kinetic data obtained at 633 K. Eqs (12) and (13) can be eliminated owing to a large error with which they describe the experimental data. Of the remaining three equations, the experimental data are approximated best by Eq. (7). However, it is important, whether it can correctly express also the effect of pressure on the reaction rate. Consequently, Eqs (7), (8), and (15) were employed for the calculation of values of reaction rates and these values were compared with experimental ones for the data measured at pressures of 0·5 and 0·9 MPa. In this calculation we used constants obtained in the pressure range 0·1 − 0·3 MPa. Results of this comparison are given in Table II and in Fig. 4 and they confirm that Eq. (7) describes best the kinetics of the reaction at elevated pressures.

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