KINETICS OF CATALYTIC CONVERSION OF METHANOL AT HIGHER PRESSURES

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The course of the conversion of methanol with water vapour was followed on a low-temperature Cu–Zn–Cr–Al catalyst at pressures of 0·2 and 0·6 MPa. The kinetic data were evaluated together with those obtained at 0·1 MPa and the following equation for the reaction kinetics at the given conditions was derived: $r = [p(CH_3OH)p(H_2O)]^{0.5} [p(H_2)]^{-1.3}$.

The kinetics of the reaction of methanol with water vapour at atmospheric pressure at 220 to 250°C on a low-temperature catalyst $CuO–ZnO–Cr_2O_3–Al_2O_3$ was described in our preceding work[1]. Its rate, r, could be expressed either by the approximate equation
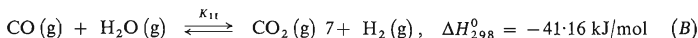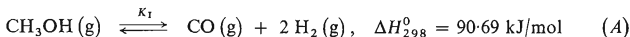
$$r = k_1(p_A p_B)^{0.5} , \qquad (1)$$

where k_1 denotes rate constant, p_A and p_B partial pressures of methanol and water vapours, or by the kinetic equation derived from the concept of Langmuir and Hinshelwood on the assumption that the rate-controlling process is the surface conversion of methanol on two centers:

$$r = k_2 K_1 K_2 p_A p_B (1 + K_1 p_A + K_2 p_B)^{-2} , \qquad (2)$$

where k_2 denotes rate constant, K_1 and K_2 adsorption constants of methanol and water vapours.

Since the studied reaction is intended to proceed in an elevated-pressure hydrogen generator for fuel cells, it was necessary to study its kinetics at higher pressures. In addition, a wider range of the partial pressures of the reaction components constitutes a better base for the experimental verification of the kinetic equation. The equilibrium data obtained by thermodynamic analysis[1] of the assumed reactions

$$CH_3OH\,(g) \; \xrightleftharpoons{K_I} \; CO\,(g) + 2\,H_2\,(g), \quad \Delta H^0_{298} = 90{\cdot}69 \text{ kJ/mol} \qquad (A)$$

$$CO\,(g) + H_2O\,(g) \; \xrightleftharpoons{K_{II}} \; CO_2\,(g) \; 7 + \; H_2\,(g), \quad \Delta H^0_{298} = -41{\cdot}16 \text{ kJ/mol} \qquad (B)$$

(Table I) suggest that an increased pressure causes a shift in the equilibrium against decomposition, nevertheless even at 1 MPa the reaction equilibrium is shifted considerably to the right side and the pressure dependence in this range can be neglected.

The catalyst and the reaction conditions are chosen according to the same rules[1-7] as at a pressure of 0·1 MPa.

EXPERIMENTAL

Apparatus and method. The reaction course was followed in an isothermal flow-integral reactor with a plug flow. The scheme of the apparatus adapted for measurements at elevated pressure

TABLE I

Equilibrium Values of x, y, and CO Content after Condensation of Unreacted Methanol and Water Vapour in Dependence on Temperature and Molar Ratio of $CH_3OH : H_2O$ at 0·5 and 1·0 MPa

x^* Denotes conversion of CH_3OH to CO in equilibrium, y^* conversion of CO to CO_2 in equilibrium.

Mol. ratio $CH_3OH : H_2O$	°C	0·5 MPa			1·0 MPa		
		x^*	y^*	% CO	x^*	y^*	% CO
1 : 1	200	0·974	0·882	2·42	0·925	0·885	1·09
	230	0·991	0·861	3·39	0·968	0·851	3·12
	250	0·996	0·835	4·21	0·984	0·830	4·07
	300	0·999	0·770	6·08	0·997	0·769	6·04
1 : 2	200	0·998	0·985	0·33	0·990	0·978	0·30
	230	0·999	0·978	0·53	0·996	0·975	0·53
	250	0·999	0·968	0·78	0·998	0·967	0·83
	300	1·000	0·938	1·62	0·999	0·936	1·60

FIG. 1

Scheme of Pressure Apparatus

1 Resevoir of aqueous methanol, 2 piston micropump, 3 reactor, 4 catalyst layer, 5 furnace, 6 thermocouple, 7 cooler, 8 manometer, 9 separator, 10 outlet valve, 12 bubble flow meter, 13 stopcock for taking samples.
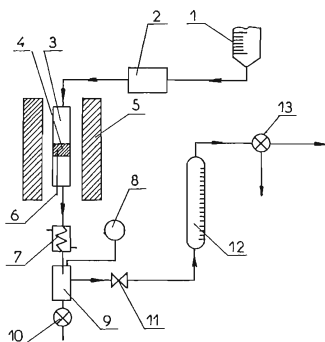
is shown in Fig. 1. An aqueous solution of methanol was continually injected by a piston micro-pump from a burette into the reactor made of steel, whose upper part served as praeheater. The reactor was placed in a block furnace with controlled heating. The temperature in the reactor was measured with an iron-constantan thermocouple placed in the catalyst bed. The catalyst was put on a stainless steel grid in the reactor and the remaining free space was filled up with ground glass particles of the same size as the catalyst. The converted gas was led from the reactor into a cooler to condense the remaining water and methanol, which were separated. The gas was further led through a regulation valve to maintain a constant pressure in the reactor, then into a thermostated flowmeter, and sten samples were taken for analysis. Carbon dioxide was determined on an Orsat apparatus, carbon monoxide on a gas chromatograph Chrom3-I (Laboratorní přístroje, Prague).

Catalyst. The reaction proceeded at increased pressure on a low-temperature catalyst for water gas conversion of the following composition: $35\cdot85\%$ CuO, $10\cdot23\%$ ZnO, $19\cdot03\%$ Al_2O_3, $2\cdot6\%$ Cr_2O_3, loss on heating at $850°C$ $23\cdot55\%$, surface area 102 m^2/g (nonreduced catalyst). The most serious problem, which complicated the kinetic measurements, was deactivation of the catalyst, which depended on the molar ratio of $CH_3OH : H_2O$ of the inlet mixture. The catalyst was most stable at a molar ratio of $CH_3OH : H_2O = 1 : 2$ and higher; it was the more deactivated the lower was the content of water vapour in the inlet mixture. Factors influencing deactivation were not studied in detail. For the experiment, 3 g the catalyst of particle size $0\cdot6$—$1\cdot0$ mm was mixed with ground glass of the same particle size in the ratio of $3 : 1$. It was reduced prior to the measurement with a mixture of nitrogen with 3% hydrogen in a reactor at 170—$240°C$ and a volume rate of flow of $3\cdot75$ dm^3 h^{-1} g^{-1} (NTP).

Determination of kinetic isotherms, i.e., the dependence of the degree of conversion y on W/F, where W denotes amount of catalyst (g) and F rate of flow of the inlet mixture (mol/h), was carried out at pressures of $0\cdot2$ and $0\cdot6$ MPa, temperatures of 220, 230, 240, and $250°C$, inlet rate of flow $0\cdot35$—$2\cdot3$ mol/h, and molar ratio of $CH_3OH : H_2O$ $1 : 1$, $1 : 1\cdot1$, $1 : 1\cdot3$, $1 : 1\cdot5$, and $1 : 2$. Examples of kinetic isotherms are shown in Figs 2 and 3.
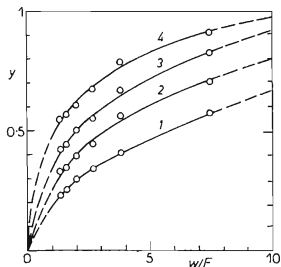
Fig. 2

Kinetic Isotherms for Molar Ratio of CH_3.
$.OH : H_2O = 1 : 1\cdot3$ at $0\cdot2$ MPa
    Temperature: *1* 220; *2* 230; *3* 240; *4* 250°C.
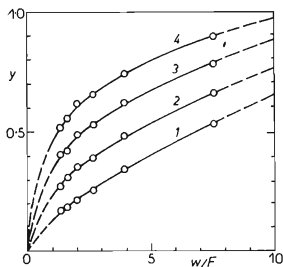
Fig. 3

Kinetic Isotherms for Molar Ratio of CH_3.
$.OH : H_2O = 1 : 1\cdot3$ at $0\cdot6$ MPa
    Temperature: *1* 220; *2* 230; *3* 240; *4* 250°C.

Treatment of data. The total degree of conversion was calculated from the rate of flow of the inlet mixture F, and rate of the reacted gaseous mixtures V and the content of CO_2 and CO according to the equation

$$y = v[z(CO_2) + z(CO)]/22 \cdot 41 Fn_0 , \tag{3}$$

where v denotes rate of flow of the reacted gas mixture (dm^3/h) (at standard conditions), n_0 mole fraction of methanol in solution, z volume percent of the corresponding component in the gas mixture after condensation of the unreacted portion of CH_3OH and H_2O. The degree of conversion to CO_2 was calculated as

$$y(CO_2) = vz(CO_2)/22 \cdot 41 Fn_0 . \tag{4}$$

The small difference between the values of y and $y(CO_2)$ was neglected. The reaction rate, defined as

$$r = n_0 \, dy/d(W/F) , \tag{5}$$

was calculated by the earlier described method[2]. The kinetic isotherms were first approximated by an empirical function of the form

$$y = 1 - (1 + a_1 x + a_2 x^2) \exp(bx) \tag{6}$$

whose differentiation gave the reaction rate:

$$r = -n_0 \exp(bx) [a_1 + 2a_2 x + b(1 + a_1 x + a_2 x^2)] , \tag{7}$$

where $x = W/F$ and a_1, a_2, b are constants whose values were calculated for the individual kinetic isotherms by nonlinear regression on a Hewlett–Packard 9830 A computer.

RESULTS AND DISCUSSION

The conversion of methanol proceeds according to the overall equation

$$CH_3OH\,(g) \; + \; H_2O\,(g) \; \rightleftharpoons \; CO_2\,(g) \; + \; 3\,H_2\,(g) . \tag{C}$$

Its main products are CO_2 and H_2, however carbon monoxide is also present in the converted mixture. Hence, the reaction proceeds by a complex mechanism and may be assumed to involve two consecutive reactions (A) and (B) as discussed earlier[1]. Also in this case the experimentally found content of CO was very small (at most $0 \cdot 6\%$) so that, as already mentioned, the total conversion of methanol, y, differs only little from the conversion to CO_2 and hence also the reaction rate of CO_2 formation differs only little from the overall conversion rate. At a maximum content of $0 \cdot 6\%$ CO, these rates differ by about 5%, hence for the sake of simplicity only the overall conversion rates of methanol were determined and used in further considerations.

As a first step, the measured data were correlated with the following empirical equation:

$$r = k_3 p_A^a p_B^b p_C^c p_D^d , \tag{8}$$

where k_3 denotes rate constant and p_i partial pressures of methanol (A), water vapour (B), carbon dioxide (C), and hydrogen (D). Its simplified form is Eq. (1), which was used[1] for atmospheric pressure and was found to describe the experimental data with a maximum deviation of 3·5%. However, for the data at higher pressure in the present work, this equation applies with an error of 15·8% and moreover the constant k_1 depends on the pressure.

For this reason, we decided to take into account the dependence not only on the starting components but also on the products, i.e., on partial pressures of CO_2 and H_2. Analysis of Eq. (8) by nonlinear regression revealed that the exponent c is negligibly small, hence the reaction is independent of the partial pressure of CO_2. The following equation is applicable at elevated pressures:

$$r = k_4(p_A p_B)^{0.5} \, p_D^{-1.3} \, .\tag{9}$$

The constant k_4 at various temperatures and the apparent activation energies are given in Table II. Data measured at 0·1 MPa were included in the evaluation.

This kinetic equation enables one to make simple calculations for various conditions, but it does not form a basis for discussing the possible reaction mechanism. The term $p_D^{-1.3}$ suggests that hydrogen acts as a hindering agent at increasing pressure, apparently owing to concurrent adsorption on the catalyst surface. Fractional exponents also suggest a complex reaction course.

Approximation of the experimental data at elevated pressure by Eq. (2) turned out unsatisfactory. This equation does not involve the inhibition effect of hydrogen, which is obvious from Eq. (9). Relations derived earlier[1], which take this effect

TABLE II

Values of k_4 in Eq. (9) at Different Temperatures in the Range 0·1—0·6 MPa and their Statistical Test

σt Product of standard deviation and critical t value for the reliability interval on a 95% level; $\overline{\Delta r_r}$ mean relative deviation of reaction rate; E^* apparent activation energy.

Temperature K	$k_4 \cdot 10^2$ mol MPa^{0,3}g^{-1}h^{-1}	$\sigma \cdot t$	$\overline{\Delta r_r}$ %
493·16	1·64	0·0030	8·81
503·16	3·41	0·0021	7·29
513·16	6·81	0·0090	7·94
523·16	10·88	0·0093	8·73

$E^* = 116.05$ kJ mol^{-1}.

into account, did not fit the experimental data with a satisfactory accuracy or the adsorption constants involved in them did not have a physical sense. The equations obviously do not take into account the relevant effects or the approximations involved are not adequate. A derivation of other equations based on the concepts of Langmuir and Hinshelwood, which would take into account all possible reaction steps, results in bulky expressions whose interpretation is problematical. Eq. (9) is suitable for calculating the reaction rate in designing a model hydrogen generator for fuel cells. The reaction mechanism has to be studied by other methods.

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Translated by K. Micka.