The Kinetics of the Water-Gas Conversion IV. influence of Alkali on the Rate Equation

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In continuation of previous investigations on the kinetics of CO conversion with water over a commercial iron oxide-chromium oxide catalyst the present article deals with a comparison of the kinetic expressions obtained with laboratory-prepared catalysts without and with alkali present in minor quantities. Quite substantial influences of the alkali on the kinetic expression were found. It was further found that CO, concentrations above a certain limit produred a relatively slow decrease of activity of the alkali-impregnated catalysts, the effect being dependent on the temperature of drying of the catalyst prior to the impregnation. Some points of theorctical interest in connection with the findings are discussed.

INTRODUCTION

Kinetic expressions of the power type were previously deduced for the CO conversion with H,O over a commercial iron oxide-chromium oxide catalyst, applying an H_2S -free gas $(1, 2)$ and H_2S -containing gas (3) . It was found that small quantities of H_2S in the feed gas considerably influence the form of the kinetic equation. Another impurity which conceivably may be encountered in connection with CO conversion is alkali, present in the catalyst and originating from the precipitation of iron hydroxide. It seemed, a priori, to be possible that the presence of alkali might influence the form of the kinetic equation, e.g., by increasing the adsorption of $CO₂$.

It was therefore decided to investigate the kinetics of the CO conversion over a laboratory-prepared alkali-free iron oxidechromium oxide catalyst and over similar catalysts impregnated with known amounts of NaOH, using an H₂S-free gas. The experiments were performed at atmospheric pressure and 380".

EXPERIMENTAL

Gases. The gases applied $(CO, CO₂, H₂)$

and N_2) were taken from cylinders and were from the same source and of the same purity as those used previously. Also the purification procedures were similar to the previous ones (1) . In view of the "poisoning" effect observed on certain of the alkali-containing catalysts by high $CO₂$ concentrations there may be reason to mention that the only impurity found to be present in the $CO₂$ is a small amount of air, the oxygen concentration not exceeding 0.01%. This oxygen content is believed not to be of essential influence. The $CO₂$ was passed over active carbon at room temperature together with the other gases. An experiment described later in this article showed that an alkali-free catalyst. was not affected by the CO₂ which produced the "poisoning" effect on the alkali-containing catalysts.

Catalysts. The alkali-free catalyst, A, was prepared in the following way: 253 g A.R. $\text{Fe}(\text{NO}_3)_3 \cdot 9$ H₂O and 15.8 g A.R. $Cr(NO₃)₃ \cdot 9$ H₂O were dissolved in 750 cm3 water. The solution was precipitated with a slight excess of $3 M$ ammonia. After filtration and thorough washing the precipitate was dried overnight at, 125°C and

again overnight at 300°C. The filter cake was broken into pieces, and the sieve fraction between 0.8-1.2 mm was used for the kinetic measurements. The nominal composition of this catalyst was 94.3% Fe₂O₃ $+ 5.7\% \text{ Cr}_2\text{O}_3.$

Several alkali-containing catalysts were prepared. Catalyst B was prepared by impregnation of catalyst A with 2.5% NaOH. The sieve fraction 0.8-1.2 mm of catalyst A was soaked in a $1 M$ NaOH solution, filtered, and dried overnight at 125[°] and again overnight at 300". After this procedure was performed twice the alkali content amounted to 2.5 wt $\%$. The amount of alkali deposited in the catalyst was calculated from the amount of NaOH solution taken up by the wet catalyst as determined from the weights of the dry and the wet catalyst. This method may not be a very exact one; however, it is good enough for the present purpose.

Catalysts C and D were prepared in the same manner, the content of alkali being 0.6% NaOH and 1.4% Na₂CO₃ (equivalent to 1.1% NaOH), respectively.

Catalyst E was different from the other catalysts in that the impregnation was performed on the precipitate after drying at 125', thus omitting the drying at 300". The alkali content was 1.9% NaOH.

A detailed investigation of the kinetics

was performed on catalysts A and E only.

The amount of catalyst used was in all cases 3.00 g (unreduced) diluted by inert material (quartz) to a total volume of 12.0 cm3. Before starting the measurements the catalyst was reduced at 300°C and thereafter stabilized by running for about 1 week at the temperature at which the measurements were intended to take place, i.e., 380°C. Further, the catalyst was kept at 420' once overnight in order to improve the stability of the catalyst during the measurements. Even the stabilized catalyst was not completely stable; however, the loss in activity was so slow that it did not seriously influence the measurements.

Experimental Set-Up. A diagram of the experimental set-up is shown in ref. (1). A schematic drawing of evaporator and reactor is shown in Fig. 1. The gases were supplied through flow meters and purification trains to the evaporator where liquid water was introduced by means of a proportioning pump. The evaporator was filled with a ceramic material. The mixture of water vapor and gases was passed through a heated tube to the glass reactor which was designed in the following way: the catalyst was placed in an inner tube (l&mm i.d.) through which an axial thermocouple tube (6-mm o.d.) passed so that the temperature might be measured at any

FIG. 1. Schematic drawing of reactor.

level of the catalyst bed, the height of which was 5.2 cm. Incoming feed gas passed through an annular space in countercurrent flow with the gas in the catalyst tube. The outer wall of the annular space was provided with a Ni-chrome heating coil. Outside the heating coil was placed a glass mantle. By manipulating the ineulation of this outer glass mantle it was possible to keep the temperature variation along the axis below 4°C between the warmest and the coldest spot.

It is somewhat difficult to obtain data for a reliable estimate of the radial temperature gradient, mainly because most investigations on radial heat transfer are concerned with conditions valid only to a limited degree for the present case. A search of the more recent literature indicates, however, that an effective thermal conductivity of the catalyst bed equal to 0.35 kcal/meter hr C is a conservative estimate. Applying this value and Damköhler's formula (4) an upper limit for the radial tcmperaturc variation is calculated to be 3°C.

Analytical procedure. $CO₂$ and CO were as usual determined in an Orsat apparatus by absorption in KOH solution and in CuCl solution, respectively. Remaining traces of CO were oxidized over CuO and absorbed in KOH solution. H_2 was determined by gas chromatography after removal of $CO₂$. The amount of dry exit gas was measured by a wet gas meter.

EVALUATION OF EXPERIMENTAL RESULTS

The degree of conversion of carbon monoxide x , has been calculated from the following equations

$$
x = \frac{(\text{H}_2)_{\text{e}} - [(\text{H}_2)_{\text{0}}/(\text{CO})_{\text{0}}](\text{CO})_{\text{e}}}{(\text{H}_2)_{\text{e}} + (\text{CO})_{\text{e}}} \quad (1)
$$

$$
x = \frac{(CO_2)_{e} - [(CO_2)_{0}/(CO)_{0}](CO)_{e}}{(CO_2)_{e} + (CO)_{e}} \quad (2)
$$

Equation (1) was applied when (H_2) ₀ was low and Eq. (2) when $(CO_2)_0$ was low. In the cases where the error obtained by the two methods were of the same order, the average value of x was applied.

Special care was necessary for the experiments where $(CO)_0$ was varied (Table 2) due to the low content of CO (and the low degree of conversion). In this case average values of x given in the table also comprise the value obtained from the following equation, which, contrarily to Eq. (2) , does not contain $(CO)_0$

$$
\boldsymbol{x} = \frac{(CO_2)_{\rm e} - (CO_2)_{\rm 0}}{(CO_2)_{\rm e} - (CO_2)_{\rm 0} + (CO)_{\rm e}[1 - (CO_2)_{\rm 0}]}\tag{3}
$$

and from the analogous equation with H_2 instead of $CO₂$. Application of several different methods of calculation of x furnishes a control of the consistency of the analytical data.

The partial pressures applied for the calculations of x are "dry" gas partial pressures. Anywhere else in this article the symbols used in Eqs. l-3 refer to "wet" gas partial prcssuree.

In the investigations described previously $(1, 2, 3)$ it appeared to be possible to express the rate by an equation of the power type

$$
r = r_f - r_b = f(dx/dw)
$$

= $k({\rm CO})^t({\rm H_2O})^m({\rm CO_2})^n({\rm H_2})^q(1-\beta)$ (4)
 $\beta = ({\rm CO_2})({\rm H_2})/K({\rm CO})({\rm H_2O})$

This was also attempted in the present case for the catalysts A and E. The catalysts B, C, and D were mainly applied for an investigation of the $CO₂$ poisoning effect described later.

The technique applied for fitting the experimental data to an equation of the type (4) was the usual enc. In each series of runs the concentration of one of the reactants or products in the feed gas was varied together with the concentration of N_2 in such a way that the sum of the concentrations N_2 and the component under consideration was kept constant. As the degree of convcrsion was not very high, a preliminary value of one of the exponents l, m, n , or q, depending on which component was being varied, could be obtained from each series by the graphic method described previously (1). After insertion of the pre-

the rate constant k which made the calcu- partial pressure and the experimental delated conversion equal to the one obtained gree of conversion. From the amount of experimentally was obtained in the follow- catalyst, W^* , thus obtained, k was calcuing way by application of the electronic lated from the relation $kW = k^*W^*$ in digital computer GIER. After insertion of which W is the actual amount of catalyst. an arbitrary (approximate) rate constant The values of l, m, n , or q were varied k^* Eq. (4) was integrated until the partial in steps of 0.05 until the values of k within

liminary values, l, m, n , and q in Eq. (4), equal to that obtained from the initial CO

pressure of any one of the components was each series showed a minimum of sys-

EFFECT OF VARIATION OF FEED GAS COMPOSITION-CATALYST A^a RATE EQUATION APPLIED: $r = k$ (CO)^{0.75}(H₀O)^{0.36}(CO₀)^{-0.35}(H₀)^{-0.05}(1 - *B*)

 43.00 g of catalyst used in each group of experiments.

			\sim (\sim)	(112V)	$\sqrt{2/2}$	(227) V	Μ.
	Feed gas composition (%)					Conv.	
Total feed (mole/hr)	$_{\rm CO}$	CO ₂	H ₂	\mathbf{N}_2	H ₂ O	$\displaystyle{\exp_x(x) \over x(\%)}$	Rate const. k
			Variation of $(CO)_0$				
2.250	18.3	3.13	6.15	52.0	20.4	11.4	0.0371
2.308	4.7	3.29	5.92	66 2	19.9	8.5	0.0422
2.263	9.5	3.19	5.82	60.9	20.6	9.3	0.0360
2.367	26.4	3.42	6.13	44.4	19.7	12.3	0.0398
			Variation of $(H_2O)_0$				
2.233	17.9	3.4	6.18	51.8	20.7	11.1	0.0369
2.392	17.8	3.2	6.08	35.1	37.8	10.2	0.0385
2.363	18.3	3.5	6.30	15.5	56.4	9.7	0.0390
2.329	17.9	3.1	6.01	43.1	29.9	10.0	0.0350
2.275	17.9	3.2	6.14	63.0	9.8	12.2	0.0368
2.350	17.9	3.2	6.13	24.0	48.8	9.4	0.0358
			Variation of $(CO_2)_0$				
2.242	19.3	$\bf{0}$	5.9	58.6	16.2	19.5	0.0442
2.313	17.7	2.3	6.38	54.7	18.9	15.0	0.0486
2.379	17.9	6.2	6.27	51.0	18.6	9.8	0.0411
2.400	18.1	9.1	6.20	48.4	18.2	9.1	0.0438
2 3 1 3	17.8	$\boldsymbol{0}$	5.7	57.6	18.9	17.9	0.0408
			Variation of $(H_2)_0$				
2.388	17.5	2.9	6.6	52.6	20.4	14.2	0.0507
2.367	17.6	3.3	0.20	58.3	20.6	14.0	0.0509
2.350	17.7	3.2	21.8	38.2	19.1	13.6	0.0489
2.396	17.2	3.0	59.1	0.4	20.3	14.0	0.0535
2.404	17.3	3.1	11.6	47.7	20.3	14.8	0.0551
2.358	17.7	3.1	38.3	20.2	20.7	13.2	0.0481

TABLE 2 EFFECT OF VARIATION OF FEED GAS COMPOSITION-CATALYST E^a RATE EQUATION APPLIED: $r = k$ (CO)1.35(H.O)⁻⁰.15(CO.)⁻⁰.40(H)0.00(1 - p)

n 3.00 g of catalyst used in each group of experiments.

tematic variation as determined by the method of least squares with the partial pressure of the component being varied.

The data obtained with catalyst A (alkali-free) are given in Table 1, and the data obtained with catalyst E (containing 1.9% NaOH) are given in Table 2. The tables contain total amount of feed gas, composition of feed gas, the degree of conversion obtained, and rate constant k . The final rate equation which has been

utilized for calculating k is given above each table.

DISCUSSION

The experiments with the alkali-free catalyst, A, did not show any extraordinary features. As appears from Table I the experimental data could be fitted satisfactorily to a power equation with the exponents $l = 0.75$, $m = 0.30$, $n = -0.35$, and $q = -0.05$. The deviation of q from 0 is so small as to be rather doubtful.

The alkali-impregnated catalysts B, C, D, and E, on the other hand, gave some unexpected results. It is quite ordinary that the degree of conversion decreases when the $CO₂$ partial pressure increases, the partial pressures of the other reactant(s) and product(s) being kept constant. This decrease in conversion is obtained almost immediately after having changed the gas composition. When applying catalyst B (2.5% NaOH), however, it appeared that by increasing the $CO₂$ partial pressure above a certain limit there occurred in addition to the fast lowering of the conversion also a slow decrease of activity. This slow decrease took place during $1-2$ days and had almost the character of a complete poisoning. By removing the $CO₂$ the former activity was regained, also in the course of l-2 days. In order to ascertain that the $CO₂$ did not contain any poison which escaped purification, catalyst B was replaced by the alkali-free catalyst A, applying the same feed gases. No slow deactivation took place at high $CO₂$ concentration.

The catalysts C (0.6% NaOH) and D $(1.4\%$ Na₂CO₃) showed the same phenomenon: a slow, but rather sharp decrease in activity when the $CO₂$ partial pressure exceeded a certain limit.

A graphical representation is given in Fig. 2, in which $\ln x$ is plotted vs. $\text{In}[(CO_2)_0+(x/2)(CO)_0].$ $(CO_2)_0+(x/2)$ \cdot (CO)₀ is the average partial pressure of $CO₂$ in the reactor. As shown previously (1) an approximately straight line with slope equal to n is obtained if a rate expression of the type of Eq. (4) is obeyed. The points in Fig. 2 which are put in parentheses represent unstable conditions. The $CO₂$ limit at which the sharp de-

crease sets in has not been determined exactly. At 380° and a gas composition of 25% CO, 25% H₂O, and 0% H₂ it seems to be in the range $10-15\%$ CO₂. At higher temperatures the limit is higher.

The catalysts B, C, and D had in com-

FIG. 2. Dependence of the degree of conversion x on the average content of $CO₂$ for catalysts B, C, and D. Composition of feed gas, except $CO₂$ and N₂: 25% CO, 6% H₂, 25% H₂O. Points in parentheses represent unstable conditions.

mon that they had been heated at 300° before being impregnated with alkali. Catalyst E (1.9% NaOH) had only been dried at 125" before impregnation with alkali. The behavior of this catalyst with respect to $CO₂$ effect was somewhat different from that of the other alkali-impregnated catalysts. As appears from Fig. 3 there is still a $CO₂$ limit above which there is a change from a less steep to a more steep decrease of activity with increasing CO, concentration. The steeper decrease, however, is much less pronounced than with catalysts B-D. It is in the logarithmic representation represented by a straight line of slope approximately 1.0. Again, the points in parentheses represent unstable conditions.

The slope of the lines (and therefore also the exponent *n*) representing low $CO₂$ concentrations seem to be approximately the same $-(0.45-0.5)$ for all of the catalysts B-E although they are not fixed with any

great accuracy. The two curves shown in Fig. 3 representing experiments with two

Fro. 3. Dependence of the degree of conversion on the average content of $CO₂$ for catalyst E. Feed gas composition (except $CO₂$ and $N₂$), Case I: 18% CO, 6% H₂, 18% H₂O; Case II: 18% CO, 6% H₂, 37% H₂O. Points marked x indicate runs made at end of series. Points in parentheses represent unstable conditions.

different $H₂O$ concentrations indicate that the critical CO, concentration is lowered with increasing $H₂O$ concentration.

Keeping the $CO₂$ partial pressure in the low concentration range catalyst E was also subjected to varying concentrations of CO, $H₂O$, and $H₂$. The experimental data are given in Table 2. The data for $(CO₃)₀$ variation correspond to the variation of $CO₂$ in the low $CO₂$ concentration range of case I, Fig. 3. It is seen that a satisfactory fitting of the experimental data to a rate expression of the power type was obtained in the concentration ranges applied. The concentration range applied for CO was also smaller than usual. This is due to the fact that at higher concentrations of CO irreversible changes in

the catalyst caused by reduction of iron oxide to pure iron occurred.

The exponents obtained with catalysts A and E are summarized in Table 3, which for comparison also contains the exponents obtained with the commercial catalyst $(1, 2)$. The exponent q apparently is independent of the alkali content. In the low $CO₂$ range the exponents *n* are also identical within experimental uncertainty for the catalysts A and E (and probably also for the catalysts B-D). On the other hand, somewhat unexpected values were found for the CO exponent, I, which appeared to be higher than one (1.35) and for the $H₂O$ exponent, m, which appeared to be negative (-0.15) for catalyst E. This result is substantiated by the fact that preliminary experiments with catalyst B indicated similar values of l and m . These findings, together with the effect of high $CO₂$ concentrations on alkali-containing catalysts, are discussed in the following.

The reaction mechanism for the catalytic CO conversion probably cannot be deduced uniquely from purely kinetic investigations because different mechanisms may well result in kinetic expressions which, due to the heterogeneity (intrinsic or inducedj of the surface, cannot be distinguished from each other. For example, the rate expression obtained for catalyst A may be considered to be an approximation of the rate expression obtained by applying the Hougen-Watson method (5) assuming the surface reaction between adsorbed CO and O to be controlling or alternatively of the expression obtained by the steady state method (6) assuming a mechanism in which reaction occurs between the gaseous components and reduced and unreduced surface sites. On the other hand, the results obtained with our catalysts cannot very well bc reconciled with the mechanism proposed by Kulkora and Temkin $(7, 8)$.

Although it is thus not, possible to give an unambiguous explanation of the differences between catalysts A and E in terms of changes in the reaction mech-

VALUES OF EXPONENTS l, m, n , and q Obtained with Different Catalysts							
		\boldsymbol{m}	п				
Catalyst A (alkali-free)	0.75	0.30	-0.35	-0.05			
Catalyst E $(1.9\%$ NaOH) (low CO ₂ -range)	$1.35\,$	-0.15	-0.40	0.00			
Commercial catalyst	$1.00\,$	0.25	-0.60	0.00			

TABLE 3 VALUES OF EXPONENTS l, m, n , and q Obtained with Different Catalysts

anism, it is, however, possible to indicate certain features which may have some bearing on the results obtained. The fact that the rate for catalyst E is more than proportional to the partial pressure of the reducing agent CO as well as negatively influenced by an increase of the partial pressure of the oxidizing agent H_2O may indicate that the activity of this catalyst is dependent on the state of oxidation of the surface layer and that a lower state of oxidation is a more active catalyst than a higher state of oxidation. In view of the zero effect of $H₂$ it should be pointed out that $H₂$ with respect to iron oxides is a much slower reducing agent than is CO. It. is, however, an open question, as to why alkali does promote such an effect.

Another, perhaps somewhat more farfetched, hypothesis to explain the fact that 1 becomes greater than one in the presence of alkali, is the assumption that some rate-determining step involves a compound containing more than one CO group. A mechanism discussed by Basolo and Pearson (9) comprising iron carbonyl and iron hydrocarbonyl in the presence of alkali might satisfy this assumption.

With respect to the cause of the $CO₂$ effect it is also only possible to make certain assumptions. The decline in activity obtained with increasing $CO₂$ concentration in the low $CO₂$ range may possibly be due to increasing coverage of the surface with adsorbed $CO₂$. The more rapid decrease at higher $CO₂$ concentrations may be due to the onset of an oxidation effect similar to that mentioned above for water. It is, however, somewhat difficult to imagine that this effect can be as violent as that encountered for the catalysts B-D. for assistance with the experiments.

Another possible way in which $CO₂$ may influence the catalytic activity of the alkali-containing catalysts is by formation of some surface compound when a certain critical CO, concentration is surpassed.

It appears from Table 3 that the kinetic expression for the commercial catalyst in some respects are closer to that obtained for catalyst A and in other respects to that obtained for catalyst E.

LIST OF SYMBOLS

- f Feed rate of CO (mole/hr)
- k Reaction rate constant for forward reaction
- K Equilibrium constant for the CO conversion
- l, m, n , and q Exponents occurring in Eq. (4)
- (CO) , $(H₂O)$, $(CO₂)$, and $(H₂)$ Partial pressures (atm) of CO, H_2O , CO₂, and H_2 , respectively. Suffix 0 indicates initial partial pressure. Suffix e indicates partial pressure at exit of the reactor.
- r Net reaction rate [mole CO converted/ $(hr) \cdot (g \text{ catalyst})$
- r_f and r_b Forward and backward reaction rates, respectively
- z Degree of conversion of CO (moles CO converted/mole CO in feed gas)
- w Weight of catalyst (g)
- β (CO₂)(H₂)/K(CO)(H₂O)

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