Oxidation of Carbon Monoxide by Oxygen on Palladium and Ruthenium Catalyst

^aJ. PÁLKA and ^bM. GREGOR

Slovchémia, General Management, Bratislava 29

^bDepartment of Inorganic Technology, Slovak Technical University, Bratislava 1

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The kinetics of carbon monoxide oxidation on palladium and ruthenium catalyst in a flow-through reactor was investigated. The formal reaction order, rate constant, and activation parameters were calculated for various compositions of the gas mixture.

Recently, the authors described the catalytic elimination of nitrogen oxide from crub hydrogen [1], in the course of which a secondary contamination of gas with carbu dioxide occurred in a plant in Slovakia. This fact stimulated the authors to study the undesirable reaction, *i.e.* oxidation of carbon monoxide by oxygen.

The oxidation of carbon monoxide with respect to industrial usage has been studie by *Brown et al.* [2]. They have, however, described neither the kinetics nor the reactive mechanism and have been mainly interested in the selection of catalyst. They use some rare metals on a carrier as catalysts. Thus they examined platinum, ruthenium and rhodium. In their laboratory experiments with palladium catalyst they came acreinteresting observations. The palladium catalyst accelerates the reaction between ongen and hydrogen

$$2\mathbf{H}_2 + \mathbf{O}_2 = 2\mathbf{H}_2\mathbf{O} \tag{(4)}$$

but even a small concentration of carbon monoxide hinders or completely stops the reaction whereas the reaction

$$2\mathrm{CO} + \mathrm{O}_2 = 2\mathrm{CO}_2 \qquad (l$$

runs in preference until the residual concentration of carbon monoxide falls to 10 p.p.t

The study of catalytic oxidation of carbon monoxide is of considerable practical impactance especially for the purification of synthesis gas necessary in ammonia production. All the papers hitherto published dealing with this problem [2-6] have been base on the demand to remove carbon monoxide from synthesis gas and therefore they a concerned with the systems containing an excess of water vapour or oxygen.

This paper treats the study of the reaction of carbon monoxide with oxygen und reverse conditions, that is, in the presence of excess carbon monoxide. This study air at stating the oxidation conditions and recommending such process parameters whit suppress this undesired reaction to the maximum degree. Since the conversion of carbon monoxide with water vapour has already been investigated (with some catalysts s least) and the relevant data have been published [3], the authors are concerned only with the reaction of carbon monoxide with oxygen.

Experimental

Preparation of Catalysts

The catalysts were prepared by saturating the carrier (alumina, number 5780, product of Chemical Works, Záluží) with a solution of palladium(II) chloride. The carrier (pellets) were crushed, the fraction of 0.8-1.0 mm was separated, dried at 120°C, and deprived of powder. The solution of palladium(II) chloride was prepared by dissolving metallic palladium in pure hydrochloric acid. The solution of ruthenium(III) oxide chloride was prepared in the Research Institute of Inorganic Chemistry, Ústí nad Labem. The dried carrier was soaked with the necessary amount of solution of the metal compound. After soaking, the catalyst was dried and immediately before use reduced in the equipment by electrolytic hydrogen at 200°C. The catalyst reduced was deep grey. The metal compounds formed a layer on grain surfaces. It is therefore obvious that the reaction must take place on the surface of catalyst and the internal structure of carrier should not play any important role in the kinetics of process.

Equipment

Nitrogen of electric bulb industry with the oxygen content below 50 p.p.m. taken from ga3-pressure vessel I (Fig. 1) was used as carrier gas. The content of oxygen was estimated analytically beforehand [7].

Carbon monoxide of sufficient purity was prepared by decomposing formic acid with phosphoric acid at $180^{\circ}C$ [8]. Water formed in this reaction was distilled from decomposition flask 2, went off together with carbon monoxide, condensed in condenser 4, and was separated in separator 5. The remainder was adsorbed on desiccant (silica gel) 6.

Carbon monoxide thus prepared was pure, did not contain any oxygen, and was contaminated only with carbon dioxide which was removed in the purification process by soda lime 11 and solid potassium hydroxide 12.



Fig. 1. Equipment.

¹. gas-pressure vessel with nitrogen (carrier gas); 2. decomposition flask with phosphoric acid; 3. dosing of formic acid; 4. condenser; 5. separator; 6. desiccant for CO (silica gel);

gas holder with CO; 8. electrolyzer; 9. accumulator; 10. rheostat; 11. U-tube with soda lime; 12. solid KOH; 13. silica gel; 14. reactor; 15., 16. flow-meters; 17. ammeter; 18. recorder of temperature; 19. heating of phosphoric acid; 20. electric heating of reactor.

Oxygen was generated in electrolyzer 8 from water acidified with sulfuric acid. was dosed by the quantity of electric current applied to electrodes. The electroly, was performed with direct current of lead accumulator 9. The quantity of current w_{i} controlled by means of slide-wire rheostat 10 and measured with precise ammeter i accurate to 0.5%. Occasionally, the oxygen content was checked analytically.

Reactor 14 was developed and made in the Research Institute of Inorganic Chemistry Ústí nad Labem. It consists of a gas preheater of spiral shape, space for catalyst, and temperature-measuring device. The reactor was heated from outside by electric furnace: which was made in the Laboratory of Measurements, Research Centre of Duslo, Šala The temperature was regulated by means of revolving autotransformer and measure with Fe-Ko thermocouple (made in the Institute of Automation, Chemoprojekt, Satal ce). The temperature was recorded with the instrument ZPA 18 accurate to 1.5%. The temperature of cold junction was measured with a laboratory thermometer.

Carbon monoxide and oxygen were dosed through capillary flow meters 15 and r calibrated with corresponding gases.

Analytical determination

The amount of carbon dioxide formed was determined by means of an Ultragas I (Wösthoff — Bochum No. 50 GL 2-1167) device which enables us to estimate carbon monoxide and carbon dioxide present in concentration 0-500 p.p.m. with reproducibility of 1% of scale range.

According to the preliminary determination of result reliability and standard deviation it has been found that three parallel measurements are sufficient for a reliability result [9].

Calculation of the contact time of gas with catalyst

The contact time of gas with catalyst was calculated from volume velocities and temp rature according to the relationship [6]

$$au = rac{3600}{V} \cdot rac{273 \, \mu}{273 + t}, ag{4}$$

where V is volume velocity in h^{-1} , t denotes temperature in °C and μ is free volume catalyst calculated from the formula

$$\mu = 1 - \frac{\text{bulk density (g cm-3)}}{\text{catalyst density (g cm-3)}}.$$

The catalyst density determined with mercury by means of a pycnometer was 0.915: ± 0.005 g cm⁻³, the bulk density of catalyst was 0.661 ± 0.015 g cm⁻³, hence

$$\mu = 1 - \frac{0.661}{0.915} = 0.278.$$

Measurements

Initially the catalyst possesses a high activity which gradually decreases and a^{fit} a few days it settles to a certain value stable for a long time. A similar phenomenon has been described by *Parravanno* [4, 5].

OXIDATION OF CARBON MONOXIDE

This study was aimed at investigating catalysts in steady state. The reaction was followed in flow apparatus at atmospheric pressure. The values were measured at a certain flow of gas through catalyst which was characterized by volume velocity. The volume velocities of 600, 1200, 2400, and $3600 h^{-1}$ were chosen by which the contact time of gas with catalyst was fixed as presented in Table 1.

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Temperature		Volume vel	locity [h ⁻¹]	
[°C]	600	1200	2400	3600
100	1.219	0.609	0.305	0.203
125	1.142	0.571	0.286	0.190
150	1.074	0.537	0.268	0.179
175	1.014	0.507	0.254	0.168
200	0.961	0.480	0.240	0.160

Contact time of gas with catalyst [s]

The dependence of carbon dioxide formation on temperature for a certain volumevelocity was arranged into tables to interpolate the temperatures of 100, 125, 150, 175, and 200°C. Then the results thus obtained were used for the calculation of formal reaction order n and overall rate constant k.

The reaction order was calculated according to the relationship [10]

$$n = \frac{\log \frac{\Delta p_1}{\Delta \tau} - \log \frac{\Delta p_2}{\Delta \tau}}{\log p_1 - \log p_2}$$
(3)

and the values of the overall rate constant according to formula [11]

$$k = \frac{\Delta p}{\Delta \tau} p^{-n}, \tag{4}$$

where Δp and τ denote the decrease in oxygen pressure in reaction mixture (or CO) and the contact time of gas with catalyst, respectively. The indices *1* and *2* refer to different initial concentrations (partial pressures) of oxygen and carbon monoxide.

The concentrations of carbon dioxide were measured in p.p.m. and expressed in 10^{-6} . atm. The values of reaction order are dimensionless numbers while the values of the overall reaction rate k possess the dimension $atm^{1-n} s^{-1}$.

On the basis of the Arrhenius equation

$$k = Z e^{-E/RT}$$
(5)

the formal activation energy E and frequency factor Z were calculated.

Results

The experiments were carried out with two catalysts, namely palladium and ruthenium. ^{catalysts}, which were laid on the carrier (alumina) in the concentration of 0.1 volume %.

Table 2

Formal reaction order n

Catalyst	Excess CO	Excess O
palladium	0.60	0
ruthenium	0	0.30

Table 3

Overall rate constant k

Catalant	Transa		C]			
Catalyst Excess	100	125	150	175	200	
palladium	$\begin{array}{c} \text{CO} \\ \text{O}_2 \end{array}$	$egin{array}{c} 1.6 imes 10^{-4} \ 2.4 imes 10^{-5} \end{array}$	$4.6 imes 10^{-4}\ 7.9 imes 10^{-5}$	$1.3 imes 10^{-3}\ 2.5 imes 10^{-4}$	$3.8 imes 10^{-3}\ 8.3 imes 10^{-4}$	$egin{array}{c} 1.1 imes 10^{-2} \ 2.6 imes 10^{-3} \end{array}$
ruthenium	${}^{\mathrm{CO}}_{\mathrm{O_2}}$	4.1 × 10-7 —	$1.5 imes 10^{-6}\ 1.8 imes 10^{-5}$	$5.2 imes 10^{-6}\ 5.7 imes 10^{-5}$	$1.8 imes 10^{-5} \ 1.8 imes 10^{-4}$	$egin{array}{c} \mathbf{6.5 imes 10^{-5}}\ \mathbf{5.6 imes 10^{-4}} \end{array}$

Table 4

Formal activation energy E [cal mole⁻¹]

Catalyst	Excess CO	Excess O ₂
palladium	-14,750	-16,150
ruthenium	-19,000	-16,850

Table 5

Frequency factor ZCatalystExcess COExcess O_2 palladium
ruthenium 6×10^4 5.8×10^3
 2.8×10^4

The experiments have shown that in the case of palladium catalyst and excess carbon monoxide the rate does not depend on oxygen concentration while in the case of ruthenium catalyst and excess oxygen the rate does not depend on carbon monoxide concentration. The calculated values of formal reaction order, rate constant, and activation parameters are presented in Figs. 2-9 and Tables 2-5.





Volume velocity 1200 h⁻¹, Pd catalyst, excess CO.



Fig. Dependence of the overall rate constant on temperature. Pd catalyst, excess CO.



Fig. 4. Dependence of CO_2 formation on temperature and initial carbon monoxide concentration.

Volume velocity 600 h⁻¹, Pd catalyst, excess O_2 . 1. 2.5% CO; 2. 6% CO.



Fig. 5. Relationship between overall rate constant and temperature. Pd catalyst, excess O_2 .



Fig. 6. Dependence of CO_2 formation on temperature and initial oxygen concentration.

Ru catalyst, excess CO.

1. $V = 3600 h^{-1}$; 2. $V = 2400 h^{-1}$;

3. $V = 1200 h^{-1}$; 4. $V = 600 h^{-1}$.



Fig. 7. Relationship between overall restriction constant and temperature. Ru catalyst, excess CO.





Ru catalyst, excess O2.

1. $V = 600 \text{ h}^{-1}$, 6% CO; 2. $V = 600 \text{ h}^{-1}$, 2% CO; 3. $V = 1200 \text{ h}^{-1}$, 3% CO; 4. $V = 1200 \text{ h}^{-1}$, 1% CO; 5. $V = 2400 \text{ h}^{-1}$, 1.5% CO; 6. $V = 2400 \text{ h}^{-1}$, 0.5% CO.



Fig. 9. Relationship between overall reconstant and temperature. Ru catalyst, excess O₂.

Discussion

The character of kinetic data and activation parameters as well as their dependence on the composition of gas mixture may be interpreted on the basis of the following ideas.

One component of the gas mixture is adsorbed on the surface of catalyst or on its active centres. That results in an increase in partial pressure of remaining gas components. This process runs until the kinetic equilibrium characterized by reaction rate is reached.

The adsorbed molecules of one component are activated and can react with other components in the gas passing along the grains of catalyst. The reaction proceeds according to one of the following schemes.

A. Adsorption of CO

1. adsorption of component	\mathbf{M}	+	CO	\rightarrow	MCO,
2. reaction with the second component	MCO	+	$1/2O_{2}$	\rightarrow	MCO ₂ ,
3. desorption of CO_2	MCO_2	\rightarrow	M	+	CO ₂ .

B. Adsorption of O₂

1. adsorption of component	M	+	$1/2O_2$	\rightarrow	MO,
2. reaction with the second component	MO	+	CO	\rightarrow	MCO ₂ ,
3. desorption of CO ₂	MCO ₂	\rightarrow	M	+	CO ₂ .

The rate of the complete reaction is limited by the slowest reaction. The covering of surface with oxygen or carbon monoxide is the most rapid reaction in any case and for this reason the oxidation rate must be limited either by the reaction with the second component or by the desorption of CO_2 and regeneration of catalyst surface. It is very difficult to resolve on the basis of measurements performed which of these processes prevails. But the following reasoning allows to decide which of the two schemes is valid for palladium or ruthenium, respectively.

The part of surface covered with oxygen atoms or carbon monoxide molecules is Θ and the part covered with carbon dioxide is Φ . Then the part of free reduced surface must be $1 - (\Theta + \Phi)$. The ratio $\Phi : \Theta : [1 - (\Phi + \Theta)]$ will be constant at a given contact time and temperature. Provided the component adsorbed on the surface Θ of catalyst has the reaction rate of zero order, this reaction rate would not depend on the concentration of this component in gas. For instance on palladium catalyst the reaction will proceed as follows: The surface Θ of catalyst is covered with CO while the surface Φ is covered with CO₂. The surface $(\Theta + \Phi)$ will not increase with increasing partial pressure of CO because at the same time the free surface $1 - (\Theta + \Phi)$ would have to decrease. The surface of catalyst is limited and in the case of excess CO the formation of CO₂ depends on the oxygen concentration in gas. Provided oxygen is in excess, it stops to be the limiting factor of reaction rate which does not depend on the change in partial pressure of CO. That is why in the presence of excess carbon monoxide the rate is

$$v_1 = k' p_{0}^n [1 - (\Theta + \Phi)],$$

but at the same time

$$v_1 = k^{\prime\prime} p_{\Omega_2}^n \Theta.$$

The rate is a function of the partial pressure of oxygen as evident from Fig. 2. Since the surfaces Θ , Φ , and $[1 - (\Theta + \Phi)]$ are constant, they may be included into the constant k and it can be written

$$v_1 = k_1 p_{\mathbf{O}_2}^n.$$

In the case of excess oxygen the term $p_{0_2}^n$ loses its limiting character and may also be included into the constant. Thus the rate equation is transformed into the form

$$v_2 = k_2.$$

In a similar way it is possible to give evidence that oxygen is adsorbed and activated on the ruthenium catalyst because the reaction is of zero order if carbon monoxide is present in excess

$$v_3 = k_3$$

Conclusion

The reaction rate on ruthenium catalyst is generally lower than that on palladium catalyst. For this reason the formation of carbon dioxide is much lower on ruthenium catalyst than on palladium or mixed catalyst. For a pure gas, that means the absence of sulfur compounds and unsaturated hydrocarbons, it is advantageous to remove N0 from gas by one-component ruthenium catalyst in order to suppress the formation of carbon dioxide. Provided the gas is contaminated with sulfur or unsaturated hydrocarbons and the palladium catalyst has to be used, it is recommended to apply minimum temperature in order to avoid the undesirable oxidation of carbon monoxide.

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