organic compounds should be taken into account when developing photocatalytic processes of practical importance.

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HYDROGENATION OF CARBON MONOXIDE ON PLATINUM METALS

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Together with methane, methanol is the main product of the hydrogenation of CO in the presence of platinum, palladium, and iridium, applied to γ -Al₂O₃, at atmospheric pressure and temperatures of 473-573 K. Dimethyl etheris also formed on platinum and palladium, while small amounts of ethanol and acetaldehyde are formed on iridium. The hydrogenation of CO in the presence of Rh and Ru leads to the formation of normal C_2-C_5 alcohols and C_2-C_5 aldehydes. Reduction of the energy of the metal-carbon bond in the platinum metals (Pd, Ir, Pt, Rh, Ru) increases their specific catalytic activity with respect to the formation of methane and oxygenated organic compounds, and increases the selectivity for higher alcohols and aldehydes.

As demonstrated in [1, 2], palladium, iridium, and platinum catalyze at atmospheric pressure the reduction of CO to methane:

> $\mathrm{CO} + 3\mathrm{H}_2 = \mathrm{CH}_4 + \mathrm{H}_2\mathrm{O}.$ (I)

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Data are also available, showing that methanol is formed in the presence of Pt/Al_2O_3 [3] and Pd/Al_2O_3 [4]:

$$CO + 2H_2 = CH_3OH,$$

Our systematic investigations of the synthesis of oxygenated organic compounds on platinum metals have shown that in the presence of Pd, Ir, and Pt, applied on γ -Al₂O₃ other oxygencontaining products are formed besides methane and methanol. A similar investigation has also been carried out on ruthenium and rhodium catalysts. A comparison of the catalytic and physicochemical characteristics of the platinum metals (Ru, Rh, Pd, Ir, Pt) revealed some general rules inherent to this group of substances, which must naturally be considered as monotypic catalysts for the hydrogenation of carbon monoxide.

The catalysts were prepared by the application of $PdCl_2$, $IrCl_3$, $RhCl_3$, $RuCl_3$, and H_2PtCl_6 from aqueous solution to γ -Al₂O₃, followed by drying in air at 383 K and reduction in a stream of H_2 (space velocity 720 h⁻¹) in a flow-through reactor at the following conditions: platinum at 723 K for 3 h; palladium at 773 K for 4 h; iridium at 753 K for 2 h; rhodium at 773 K for 1 h; ruthenium at 723 K for 2 h and then at 773 K for 1 h. The obtained catalysts contained: 2.5 mass % Pd, 10% Ir, and 2% Pt, Rh, and Ru. The following weights were taken for the work: 0.48 g (Pd); 0.26 g (Ir); 0.42 g (Pt); 0.15 g (Rh); and 0.56 g (Ru); the surface of the metals corresponding to these weights, determined by the chemisorption of oxygen [5], was 1 m² (Pd, Ir, Ru) and 0.5 m² (Pt, Rh). The bulk volume of the palladium and platinum catalysts was equal to 1.2 cm³, of the iridium catalyst 1.8 cm³, of the rhodium catalyst 0.35 cm³, and of the ruthenium catalyst 1.4 cm³. The grain diameter of the samples was 0.25-0.50 mm (Pd, Pt, Rh, Ru) and 0.5-1.5 mm (Ir). The catalytic reaction between the carbon monoxide and hydrogen was carried out in the same flow-through reactor at atmospheric pressure, a ratio CO:H₂ = 1:3, and at temperatures 470-590 K (palladium), 530-630 K (iridium), 473-573 K (platinum), and 430-580 K (rhodium and ruthenium). The contact time was 0.35-2.6 sec. The summary degree of CO conversion at these conditions did not exceed a few per cent, because the reactor can be considered as a differential reactor.

Traces of H_2O , CO_2 , and O_2 were removed from the gases by passage through a column packed with the palladium catalyst (2 mass% Pd/SiO₂) at 380 K and columns packed with ascarite (for the absorption of H_2O and CO_2), followed by freezing out in traps at 170 K (for CO) and 81 K (for H_2). The chromatographic analysis of the reaction mixtures was performed on Biokhrom-1 and Chrom-5 chromatographs. Methane was analyzed on a capillary column (I = 50 m, phase PEG-40, T = 323 K) by taking a gas sample and quantitative determination from the peak heights with the use of a calibration graph. The oxygenated organic compounds were frozen out in a trap at 81 K for 1-3 h and analyzed on two capillary columns with different phases (PEG-40 and OV-101) by the internal standard method (with n-propanol or isobutanol).

The temperature function of the methanol formation rate on the catalysts Pt/Al_2O_3 , Pd/Al_2O_3 , and Ir/Al_2O_3 is shown in Fig. 1. The activity of the metals with respect to the synthesis of CH₃OH decreases in the order

$$Pt > Pd > Ir,$$
(III)

whereby the passage of the rate of reaction (II) through a maximum is characteristic for these catalysts. When investigating the hydrogenation of CO to methanol on Pd/Al_2O_3 it was noticed that the activity of theused catalyst is somewhat higher than that of the freshly prepared catalyst (curves 2,2' in Fig. 1). Dimethyl ether is formed on the catalysts studied (Pt, Pd) in small amounts, besides methane and methanol, as well as ethanol and acetladehyde (on Ir) (see Fig. 2).

According to [2, 6], equilibrium chemisorption of the initial reactants takes place in the hydrogenation of carbon monoxide on metals of the VIII group of the periodic system at not very high CO:H₂ ratios in the gaseous mixture (CO is adsorbed in the form of molecules, hydrogen in the form of atoms); they react chemically with the formation of a surface complex ZCHO (Z is the metal atom). The limiting stage of methane formation is the addition of adsorbed hydrogen to this complex:

$$Z CHO + ZH \rightarrow ZX_0 \xrightarrow{nZH} > CH_a, \tag{IV}$$

where ZX₀ denotes an intermediate compound which can be identified as ZC (with the liberation of H_2O) or as ZCHOH (the enol form of formaldehyde) [6]. In the case of such a mechanism the

(II)



Fig. 1

Fig. 2

Fig. 1. Rate of methanol formation as function of temperature: 1) Pt/Al₂O₃; 2,2') Pd/Al₂O₃ (2 - freshly prepared catalyst; 2') catalyst used for a long period of time); 3) Ir/Al₂O₃.

Fig. 2. Rate of formation of dimethyl ether on catalysts Pd/Al_2O_3 (curve 1) and Pd/Al_2O_3 (curve 2), and of ethanol (curve 3) and acetladehyde (curve 4) on Ir/Al_2O_3 as function of temperature.

catalytic activity of the metals with respect to reaction (I) must decrease with the increasing heat of adsorption of carbon monoxide q_{CO} [6]. According to [2], the value of q_{CO} , obtained from kinetic data on the hydrogenation of CO on metals of group VIII, increases in the order:

$$Ru < Co < Rh < Ni < Pt < Ir < Pd.$$
(V)

Accordingly, platinum, iridium, and palladium possess among the metals of group VIII the lowest specific activity in the conversion of CO to methane [2, 6].

The same order of activity (III) is also observed in the synthesis of methanol (Fig. 1). This agreement can indicate that also in reaction (II) the value of q_{CO} determines the change in activity in the transition from one catalyst to the other, although the mechanisms of CH₄ and CH₃OH formation can differ.

In the conversion to methane the intermediate compound ZX_o represents evidently a surface carbide which undergoes stepwise hydrogenation:

 $ZC \xrightarrow{2ZH} ZCH_2 \xrightarrow{2ZH} 3Z + CH_4.$ (VI)

In the synthesis of methanol the complex ZX₀ represents most probably the enol form of formaldehyde which reacts with adsorbed hydrogen:

$$ZCHOH \xrightarrow{22H} ZCH_3OH \rightarrow Z + CH_3OH.$$
(VII)

Since platinum, iridium, and palladium are at the end of the order (V), i.e., the energy of the metal-carbon bond in their case is high, the probability of carbon monoxide attaching itself to ZX₀ with the formation of a C-C bond on these metals is low. This explains the absence of compounds with C-C bonds in the products of CO hydrogenation on platinum and palladium catalysts. In the case of iridium small amounts of such compounds (ethanol and acetaldehyde) have been found. Evidently, due to higher temperatures of catalysis, due to the low catalytic activity of iridium, the probability of rupture of the metal-carbon bond increases and the following reactions become possible:

$$ZCHOH + ZCH_2 \rightarrow CH_3CHO + 2Z,$$
 (VIII)

$$ZCH_{3}OH + ZCH_{2} \rightarrow C_{2}H_{5}OH + 2Z.$$
(IX)

The condensation of methanol to dimethyl ether is a heterolytic process, the rate of which increases with increasing surface acidity [7]. Among the metals of group VIII platinum is

most electronegative [8], i.e., it possesses the highest acidity; this is apparently the cause of the increased activity (see Fig. 2) of this metal in the reaction

$$CO + 2H_2 \rightarrow CH_3OH \xrightarrow{CH_3OH} - H_2O \Rightarrow CH_3OCH_3.$$

The rates r, of formation of different products on the catalyst Rh/Al_2O_3 as function of temperature are shown in Fig. 3 (composition of the initial mixture: $P_{CO} = 25$ kPa, $P_{H_2} = 75$ kPa, flow rate 50 cm³/min). Besides the reactions (I), (II) for the formation of C₁ products (methane and methanol), products of the hydrocondensation of carbon monoxide are obtained (ethanol, acetylaldehyde and asmall amount of the C₃ alcohol n-propanol). The main oxygenated product is ethanol.

The range of products obtained from the synthesis gas on the ruthenium catalyst is even more varied (Table 1); in this case reactions for the formation of normal C_3-C_5 alcohols and C_3-C_6 aldehydes also occur, besides processes (I), (II), (VIII), and (IX).

Let us consider the rate r of summary conversion of carbon monoxide. Since methane is the predominant product at the conditions studied, the comparison of the values of r is practically equivalent to the comparison of the rates of reaction (I). The specific rates r (calculated for 1 m² of metal) on different platinum metals at the above composition of the gas mixture and equal flow rates as function of temperature are shown in Fig. 4 in Arrhenius coordinates. The obtained activation energies (Table 2) are in general agreement with the data obtained in [1, 2]. It can be seen that the catalytic activity of the metals, measured by the rate r_T at constant temperature (526 K) or by the value, reciprocal to the temperature T_r, at which an equal value of r (5•10⁻⁶ mole/m²•sec) is reached, decreases in the order

$$Ru > Rh > Pt > Pd > Ir.$$
(X)

It follows from the mechanism (IV) that an antibatic relationship must exist between q_{CO} and the catalytic activity r (at sufficiently high surface coverages with carbon monoxide) [6]. Such a relationship is in fact observed (Fig. 5) and this fact can be viewed as an explanation for the order (x).

An important characteristic of the hydrogenation of CO is the ratio of the selectivities for methane (S_{CH_4}) and the sum of oxygenated compounds (S_0) . This correlation depends on the differences in the composition, structure, and reactivity of the key intermediate compound ZX₀, formed in reaction (IV). The selectivity of the oxygenated compounds depends on the correlation between the rates of the stages:

$$ZCHOH \xrightarrow{r'}{-H_{2}O} > ZC, \qquad (XI)$$

$$ZCHOH + ZH \xrightarrow{r^*} ZCH_2OH + Z, \qquad (XII)$$

i.e.,

$$S_{O} = r''/(r' + r'') = k''/(k' + k'') = 1/(1 + k'/k''), \tag{1}$$

where k' is the rate constant of stage (XI) and k" the rate constant of stage (XII). According to the correlation of linearity of free energies (correlation of Bronsted and Temkin) the differences in the variations of these constants when varying the chemical nature of the metal are determined by differences in the energies of the metal-carbon bond in compounds ZC and ZCHOH. Evidently, the order (multiplicity factor) of this bond is higher in the first case. It can be expected therefore that the reaction (XI) will predominate the more, the higher the energy of the Z-C bond (E_{Z-C}), i.e., the ratio k'/k" will increase and the selectivity for the oxygenated products decrease (Eq. (1)).

The values of E_{Z-C} are unknown for all platinum metals; however, if we take the changes in the heat of adsorption of CO (the energy of the Z-CO bond) as a measure for the change in E_{Z-C} , we obtain the order (see Table 2):

$$Ru < Rh < Pt < Ir < Pd$$
.

Based on this we can assume that the ratio k'/k" for the three last metals ($q_{CO} = 137-153 \text{ kJ/mole}$) will be much higher than that for the first two metals ($q_{CO} = 53-82 \text{ kJ/mole}$); correspond-



Fig. 3. Rates of formation r_i (mole CO/sec·m² metal) of oxygenated compounds in the hydrogenation of CO on Rh/Al₂O₃ as function of temperature: 1) methane; 2) methanol; 3) ethanol; 4) acetaldehyde; 5) methyl acetate; 6) n-propanol.

Fig. 4. Arrhenius diagram for the rate of summary CO conversion at $P_{CO} = 25$ kPa and $P_{H} = 75$ kPa on the investigated catalysts.

TABLE 1. Distribution of Products in the Hydrogenation of CO on ${\rm Ru}/{\rm Al}_2 O_3$

Hydrogena- tion prod- ucts	Formation rate r ^{10¹⁰} , mole/(m ² ·sec)					Distribution of oxygenated compounds, mole %				
	430 K	450 K	470 K	490 K	510 K	430 K	450 K	470 K	490 K	510 K
	20	190	210	1340	9480			_		
	04	120	07	2.6	5.4	19.2	15.8	8.1	4.7	6.0
C.H.OH	0,4	0,4	34	22.0	38.0	29.7	36.8	39.4	40,7	42,3
C.H.OH	0,0	0,5	0,4	3.4	6.8	5.5	5.6	7.3	6,3	7,6
C.H.OH	0.2	0.2	0,7	3.2	2.4	10.0	9,4	8,2 °	5,8	2,7
C-H. OH	0,2	04	1.3	5.8	2.7	9.3	15,4	14,9	10,7	2,9
CH CHO	0.4	04	07	5.2	14.1	22,0	15,4	7,7	9,6	15,7
C ₄ H ₄ CHO			0.2	3,4	8,3		· · · ·	2,5	6,3	9,2
C ₄ H ₂ CHO			0.3	3.0	5,0	مب د		2,9	5,6	5,6
C.H.CHO	_	-	0,4	3,1	2,5	<u> </u>		4,5	5,7	4,5

TABLE 2. Catalytic Activity of Platinum Metals Applied on γ -Al₂O₃ in the Hydrogenation of CO*

Metal	$r_{T} \cdot 10^{8}$ mole/(m ² · sec) (T = 526 K)	Temperature at which r = 5.10 ⁻³ mole/ (m ² ·sec) is reached T _r , K	¹⁰³ /T _r , K ⁻¹	<i>E</i> , kJ/mole	9CO> kJ/mole [2,9]
Ir	0,18	602	1,66	114	148
Pd	1,32	555	1,80	103	153
Pt	3,98	532	1,88	84	137
Rh	20,9	493	2,03	89	78—82
Ru	155,0	469	2,13	128	53—54

$$*P_{CO} = 25 \text{ kPa}, P_{H} = 75 \text{ kPa}.$$

ingly, in the case of Ru and Rh the selectivity for oxygenated compounds will be higher than in the case of Pt, Ir, and Pd. The experimental data are in qualitative agreement with this conclusion: the formation of alcohols and aldehydes is more characteristic for Ru and Rh (see Fig. 3, Table 1) than for Pt, Ir, and Pd [1], which are typical catalysts for the conversion to methane.



Fig. 5

Fig. 6

Fig. 5. Correlation between the heats of adsorption of CO and the catalytic activity of platinum metals in reaction (I): O) comparison of r_T ; A) comparison of T_r (see Table 2), and the selectivity for methanol (Φ) and for the sum of alcohols C_n ($n \ge 2$) (Φ); T = 500 K for Pd, Pt, Rh, Ru, and 533 K for Ir.

Fig. 6. Application of the distribution rule of Schultz and Flory to the hydrogenation of CO on Ru/Al_2O_3 to n-alcohols at 430 K (O) and to n-aldehydes at 510 K (Δ).

It is of interest to establish and interpret the rules governing the distribution of the different oxygenated products as function of the chemical nature of the metal catalysts (experimental data on this distribution for Rh and Ru are given in Fig. 3 and Table 1). The selectivity values in Table 1 correspond to the concept of partial selectivity for the i-th product $(S_i^{(p)})$, which is equal to the ratio of the formation rate of the i-th product (r_i) and the summary rate of formation of all oxygenated substances (r_0)

$$S_i^{\rm p} = (r_i/r_0) \cdot 100.$$
 (2)

Let us supplement the mechanism (XII) with stages that reflect the formation of products C_2 , C_3 , etc. Since the nature of these stages has not yet been revealed, let us assume that C_2 products are formed in the reaction of adsorption complexes C_1 (ZCHOH, ZCH₃OH) with carboncontaining particles ZCH_x, formed in the complex stages (IV) and (VI). On the other hand, C_3 products are obtained by the introduction of ZCH_x into adsorbed C_2 particles, etc. The following conversion chains are obtained which continue reaction (XII):

$$\begin{array}{c} CH_{3}OH & CH_{3}CH_{2}OH \\ ZCHOH & \xrightarrow{2ZH} > ZCH_{3}OH & \xrightarrow{ZCH_{x}} > ZCH_{3}CH_{2}OH & \xrightarrow{ZCH_{x}} > \dots \end{array}$$
(XIII)
$$\begin{array}{c} CH_{3}CHO & CH_{3}CH_{2}CHO \\ \hline CH_{3}CHO & CH_{3}CH_{2}CHO \\ \hline ZCH_{x} & > ZCH_{3}CHO & \xrightarrow{ZCH_{x}} > ZCH_{3}CH_{2}CHO \\ \hline \end{array}$$

It follows from this scheme that the stronger the particles CH_x are bound to the surface, the less the probability of their introduction into C_1 complexes, i.e., the higher their selectivity for methanol. If we assume (as was done above) that the energies of the Z-C and Z-CO bonds correlate with each other, we arrive at the conclusion that $S_{CH_3OH}^p$ will increase with increasing heat of adsorption of CO. Such a relationship is actually observed (Fig. 5), where-by Pt, Ir, and Pd show the highest selectivity for methanol, characterized by the highest values of q_{CO}^{-} . On the other hand, higher alcohols are formed with the highest selectivity on Rh and Ru which have the lowest q_{CO}^{-} .

The selectivity for the individual members of a homologous series of products in the case of mechanism (XIII) must obey the distribution rule of Schultz and Flory:

$$\lg C_n = \operatorname{const} + n \lg \alpha, \tag{3}$$

73

where n_{i} is the number of carbon atoms in the molecule of the homolog, C_{n} is the concentration of this homolog in mole %, and α is the ratio of the rate of chain propagation (r_{nr}) to the sum of the rates of chain propagation and termination (r_{ter}) . For instance, in scheme (XIII) the rate of the methanol desorption stage (ZCH₃OH \rightarrow Z + CH₃OH) is equal to r_{ter} and the rate of the stage of interaction of ZCH₃OH with ZCH_x to r_{pr} . Figure 6 shows that the correlation (3) is achieved satisfactorily for normal aliphatic aldehydes ($\alpha = 0.51$) and somewhat less satisfactorily for alcohols ($\alpha = 0.56$). At elevated temperatures the concentration of methanol becomes lower than that of ethanol; this indicates the appearance of a systematic deviation from distribution (3). Evidently, the adsorbed methanol starts to enter into additional (with respect to scheme XIII) reactions for the formation of esters; this reduces its concentration more than would correspond to correlation (3). In fact, small amounts of ethyl acetate have been detected in the catalysis on Rh/Al₂O₃.

The correlations established in the present work may assist in the improvement of the existing and the selection of new catalysts for the synthesis of oxygenated compounds from CO and H2.

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