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Metal Carbonyl Catalysts of the Synthesis of Organic Compounds from Carbon Monoxide and Molecular Hydrogen

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Studies on the synthesis of organic compounds from carbon monoxide and hydrogen in the presence of catalysts obtained by the thermal decomposition of metal carbonyls on inorganic carriers are examined. The characteristic features of the interaction of various metal carbonyls with the carriers and the mechanisms of the formation of the metal carbonyl catalysts are discussed. The bibliography includes 165 references.

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I. INTRODUCTION

The catalytic syntheses based on carbon monoxide and hydrogen constitute the basis of industrial methods of preparation of hydrocarbons and also of a number of oxygen-containing products. A vigorous search for active and selective catalysts capable of effecting these promising processes, which make it possible to obtain valuable compounds, including the components of motor fuels based on a non-petroleum raw material, is being vigorously prosecuted at the present time in our country and abroad.[1]

A new trend in this field involves the application of catalysts based on metal carbonyls. These catalysts can be divided into three main groups: the metal carbonyl systems proper, usually employed under the conditions of homogeneous catalysis, heterogenised complexes of transition metals, and catalysts obtained by depositing metal carbonyls on carriers with their subsequent decomposition. The application of catalysts of the first two types in the synthesis of hydrocarbons from CO and H_2 has been described in detail by the present authors[2] and their application in the synthesis of oxygen-containing compounds has been described by Dombek.[3]

The present review deals with catalysts of the synthesis of organic compounds from CO to H_2 obtained by decomposing metal carbonyls deposited on various carriers. The first studies on these lines were carried out 8–10 years ago. The number of publications devoted to this problem has continuously increased in recent years.

II. THE INTERACTION OF METAL CARBONYLS WITH THE SURFACES OF CARRIERS

The decomposition reactions of metal carbonyls on carriers and the catalyst formation reactions have been examined in a review.[4] Certain data concerning the mechanism of the interaction of metal carbonyls with inorganic carriers and also the catalytic properties of systems obtained by decomposing deposited metal carbonyls have been published.[4-6]

Inorganic carriers such as Al_2O_3, SiO_2, MgO, TiO_2, aluminosilicates, and zeolites are normally used to prepare the metal carbonyl catalysts. In certain cases the surfaces of the carriers are modified by functional groups (NR_2, PR_2, etc.) which are capable of being coordinated to the transition metal.

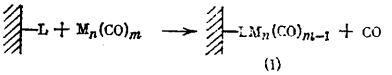
Two methods of synthesis of metal carbonyl catalysts are most widely used.[4] The first is based on the impregnation of the carrier with a solution of the carbonyl complex, usually in an organic solvent, with subsequent drying of the catalyst. In this case it is possible to obtain catalysts with any metal content, but at a high metal concentration the structures of the surface complexes obtained are as a rule inhomogeneous.

The second method is based on the adsorption of the metal carbonyl on the surface of the carrier from the gas phase or an organic solvent. Here the maximum content of the transition metal in the catalyst is determined by the adsorption capacity of the surface of the carrier used. In this instance the structure of the surface complex formed is more homogeneous.

Both methods of synthesis of the metal carbonyl catalysts are fairly universal and can be employed for virtually any types of carbonyl complexes as well as carriers.

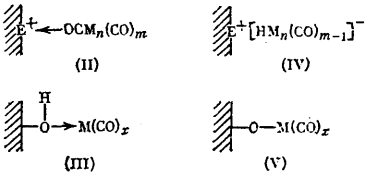
In a general form, the interaction of carbonyl complexes with the carrier surface can be described by the following schemes.[7]

(1) The substitution of CO or another ligand in the coordination sphere of the carbonyl complex by a functional group of the modified carrier:



(I)

(2) The interaction of the carbonyl complex with Lewis (E^+) or Brønsted centres on the surface of the unmodified oxide carrier with formation of various immobilised complexes:



(II) (IV) (III) (V)

Account must be taken of the fact that the interaction of the complexes with the carrier surfaces is described only approximately by the schemes presented above. The carbonyl complexes of transition metals readily react with acid or basic agents and the carrier surfaces as a rule contain a wide range of the corresponding functional groups. There is therefore a possibility of the parallel chemisorption of metal carbonyls on various surface centres with formation of several types of structures.

The interaction with a carrier may be accompanied by the decomposition of the carbonyl cluster or, conversely, by the formation of polynuclear cluster structures from mononuclear complexes. The occurrence of such processes greatly complicates the selective preparation of complexes of a specific type fixed on the carrier surface.

It must be emphasised that the direct interaction of the complexes with the active centres on the surface is of decisive importance only when the number of molecules of the carbonyl complex is comparable to the number of chemisorption centres on the carrier surface, i.e. virtually only for "low percentage" deposited metal catalysts. Otherwise the process is complicated still further as a consequence of the physical absorption of the carbonyl complexes on the outer surface and in particular within the carrier pores.

It is known[6] that the number and ratio of the Lewis and Brønsted centres on the surfaces of inorganic carriers depends greatly on the conditions of their preliminary treatment. Therefore, depending on the methods of preparation from the same initial reagents, it is possible to obtain catalysts having a different structure of the surface carbonyl complexes. IR spectroscopy is usually employed together with other physicochemical methods to investigate the mechanism of the interaction of carbonyl complexes with carriers and also the structures of the surface complexes produced.[4,6]

Account must be taken of the fact that the catalytic properties of the given systems have been studied to the greatest extent in reactions at temperatures below 200 °C (hydrogenation, isomersation, metathesis of olefins, etc.), for which a partial or complete decompostion of the surface carbonyl complexes does not occur. On the other hand, the syntheses of organic compounds from CO and H_2 normally require the application of higher temperatures. Therefore, after the deposition of the metal carbonyl on the carrier, the catalyst is in this case subjected to a preliminary heat treatment (*in vacuo* or in an atmosphere of CO, H_2, He, or a mixture of gases) in order to carry out a complete or partial decomposition of the complex and to form deposited metal particles (in an oxidised or reduced state). However, we may note that the carbonyls decompose also in the initial stages of the synthesis of CO and H_2 directly in the atmosphere of the synthesis gas.

1. Group VI Metal Carbonyls

The thermal decomposition of Group VI metal carbonyls has been investigated[9–31]) on various inorganic carriers by IR,[9–11,14,17,19,25,26,30] EPR,[10–12,19,21,22,27,28] NMR,[18] and XPE† spectroscopy[15] and by the thermoprogrammed decomposition method[13,16,20,21,23,31] (Table 1). The formation on chemisorption of the carbonyls of the surface complexes $M(CO)_5$ (ads), which exist at 20–40 °C [structure (III)][9,10] may be included among the general features of the given process. At temperatures of about 100 °C, the subcarbonyl species $M(CO)_3$(ads) are formed on the Al_2O_3 surface from molybdenum and tungsten carbonyls.[10,18–21] Such complexes have not been observed on the SiO_2 surface.[13] It has been suggested[14] that the stability of the subcarbonyl species increases with decrease in the acidity of the surface OH groups of the carrier. At 200 °C and above the carbonyl complexes decompose irreversibly with formation of oxidised forms of the metal.

In the general case the decomposition of the Group VI metal carbonyls on Al_2O_3 can be represented by the scheme[10,19]

$$M(CO)_6 + Z{-}OH \xrightarrow[-CO]{60^\circ} (Z{-}OH)M(CO)_5 \xrightarrow[-CO]{100^\circ} \rightarrow (Z{-}OH)_x M(CO)_3 \xrightarrow[-CO]{200^\circ} (Z{-}O^-)_x M^{x+} + H_2$$

This scheme includes the chemisorption of the metal carbonyls on the carrier surface, partial decarbonylation with formation of subcarbonyls at higher temperatures, and finally the complete decarbonylation and oxidation of the metal by the protons of the surface OH groups. The carriers (SiO_2, Al_2O_3) employed in the above studies were as a rule subjected to a preliminary vacuum treatment at temperatures of about 400 °C. If Al_2O_3 is subjected to a preliminary heat treatment at 950 °C, the interaction of the carbonyl with the surface proceeds differently: the decomposition of the carbonyl at temperatures above 200 °C leads to the formation of metallic molybdenum[21,23,24] or tungsten.[31] This has been explained by the appreciable decrease in the concentration of the surface OH groups in the course of the preliminary high-temperature treatment of the carrier, which stabilises the metal in the reduced state.

Table 1. The state of the metals in the thermal decomposition of chromium, molybdenum, and tungsten carbonyls on different carriers.

Initial carbonyl	Carrier	*T*, °C	State of the metal
$Cr(CO)_6$	Al_2O_3 [9,10], SiO_2 [9]	20—40	$Cr(CO)_5$ (ads.)
	Al_2O_3 [10,11], SiO_2 [12,13]	200	Cr^{2+}, Cr^{3+}
$Mo(CO)_6$	Al_2O_3 [9,14—19], SiO_2 [9]	20—40	$Mo(CO)_5$ (ads.)
	Al_2O_3 [14—16, 18—21]	100	$Mo(CO)_3$ (ads.)
	Al_2O_3 [11,14, 19—24], SiO_2 [13,14, 22,25], MgO [14], HY zeolite [26-29]	200	Mo^{3+}, Mo^{5+}
	Al_2O_3* [21,23,24], NaY [26,27]	200—500	Mo^0, Mo^{2+}
$W(CO)_6$	Al_2O_3 [9,10], SiO_2 [9,30]	20—40	$W(CO)_5$ (ads.)
	Al_2O_3 [10,31]	100	$W(CO)_3$ (ads.)
	Al_2O_3 [10,11,31], SiO_2 [12,13]	200	W^{4+}, W^{5+}
	Al_2O_3* [31]	>200	W^0

*Al_2O_3 dehyrated at 950 °C.

Analogous results have been obtained in the study of Mo-zeolitic catalysts. The decompostion of $Mo(CO)_6$ adsorbed on a type HY zeolite leads to the formation of oxidised forms of molybdenum.[26–29] On the other hand, an NaY type zeolite, containing a smaller number of OH groups, stabilises molybdenum in the zerovalent state.[26,27]

The degree of dispersion of the active component has a considerable influence on the catalytic properties of the deposited systems. Unfortunately the degree of dispersion of the metal has been determined only in a few studies. The decomposition of $Mo(CO)_6$ deposited on Al_2O_3, subjected to a preliminary heat treatment at 950 °C, leads to the formation of Mo clusters 40 Å in diameter with an overall formal charge on the metal of +0.3.[23] In contrast to metallic molybdenum, these particles do not absorb nitrogen. The authors suggest that, in the course of the decomposition of the molybdenum carbonyl on the carrier surface, Mo^{2+} ions are formed initially and then become centres for the crystallisation of zerovalent molybdenum. Such electron-deficient molybdenum clusters differ in their properties from metallic molybdenum.[23] These differences can be caused also by the different degrees of dispersion of the metal on the catalyst surface.

Thus catalytic systems containing reduced molybdenum and tungsten can be obtained by decomposing molybdenum and tungsten carbonyls on Al_2O_3 or a type NaY zeolite.

†X-Ray photoelectron spectroscopy (Ed. of Translation)].

It must be emphasised that such systems cannot be obtained from inorganic molybdenum and tungsten compounds by their reduction with hydrogen.

2. Iron Carbonyls

Numerous studies have been devoted to the interaction of complexes of iron carbonyls with the carrier surface and also to the decomposition of the surface complexes in order to obtain iron catalysts[32–57] (Table 2). The special interest in systems of this kind is due to the fact that the iron catalysts are used in industrial syntheses of hydrocarbons from CO and H_2, the synthesis of ammonia, the preparation of hydrogen, etc. IR,[32,33,35,36,38,41–43,46,47,52,54] EPR,[33,41] UV,[38,39,52] NMR,[34] and Mössbauer spectroscopy[40,41,43,55,57] and the thermoprogrammed decomposition method[39,41,42,44,50,51] are used to investigate the deposited iron carbonyl system. Since the iron carbonyl complexes are unstable in air, the systems are studied *in vacuo* or in an inert gas atmosphere.

Table 2. The state of the metal in the thermal decomposition of iron carbonyls on different carriers.

Initial carbonyl	Carrier	T, °C	State of the metal
$Fe(CO)_5$	Al_2O_3 (Refs.32, 33), MgO (Ref.32), HY zeolite (Ref.34–36), NaY zeolite (Refs.35–37)	20—40	$[HFe_3(CO)_{11}]^-$ or cluster Fe carbonyls
$Fe_2(CO)_9$	NaY zeolite (Ref.38)	20—40	»
$Fe_3(CO)_{12}$	Al_2O_3 (Refs.32, 33, 39), MgO (Refs.32, 40, 41), HY and NaY zeolites (Ref.42), SiO_2 (Ref.39), aluminosilicate (Refs. 43, 44)	20—40	»
$K_2[Fe_3(CO)_{11}]$	Al_2O_3 (Ref.45)	20—40	»
$Fe(CO)_5$	MgO* (Ref.46)	20—40	$[Fe(CO)_4]^{2-}$
$K_2[Fe(CO)_4]$	Al_2O_3 (Refs.47–49), SiO_2 (Refs.47, 48)	20—40	»
	Al_2O_3 (Refs.50, 51); MgO (Ref.46); HY and NaY zeolites (Refs.35–37, 42, 52), TiO_2 (Refs.4, 53)	40—200	$[Fe(CO)_{1-3}]_x$ (ads.)
$Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$	Al_2O_3 (Ref.54), HY zeolite (Refs.34–36, 42), TiO_2 (Ref.53), aluminosilicate (Refs.43, 44, 56)	100—300	Fe^{2+}, Fe^{3+}
	Al_2O_3 (Ref.33, 39, 47, 50, 51, 54, 55) MgO (Ref.40)	100—300	Fe^{2+}, Fe^0
	MgO* (Ref.46), NaY zeolite (Refs.35, 36, 42), graphite (Ref.37)	100—300	Fe^0

*MgO dehydrated at 800 °C.

The iron carbonyl complexes are extremely reactive. Their distinctive feature, compared with Group VI metal carbonyls, is their ability to form stable cluster structures on the carrier surface. The mechanism of the interaction of iron carbonyls with the surfaces of inorganic carriers is complex. However, it is possible to note a number of common features characteristic of these systems.

The interaction of $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ with oxide carriers leads to the formation of carbonyl clusters containing three or four iron atoms on the surface.[32–44] Mononuclear complexes of the type $[Fe(CO)_4]^{2-}$ have been identified only for MgO dehydrated at 800 °C [46] and on Al_2O_3 promoted with potassium.[47–49]

It has been suggested[32,38–42] that iron carbonyls are chemisorbed on the carrier with formation of structures of types (II) and (III). As a result of this interaction, the mononuclear iron carbonyls trimerise with formation of carbonyl clusters. The stabilisation of the mononuclear complexes on MgO and Al_2O_3 is apparently caused by the appreciable decrease in the concentration of the surface OH groups as a result of the preliminary treatment or modification of the carrier.[46–49] Thus, regardless of the type of carriers and also the initial iron carbonyls, complexes having cluster structures are stabilised on the surface in most cases.

The study of the thermal decomposition of the surface carbonyl complexes *in vacuo* or in an inert gas atmosphere showed that, up to 200 °C, stable subcarbonyl species exist on the carrier surface (Table 2). The structure of these surface complexes has been studied inadequately. They are formed on decarbonylation of the initial complexes and in certain cases the process is reversible. Treatment with carbon monoxide regenerates the initial carbonyl complexes on the carrier surface.[34,37,42,43,46] Thus one of the characteristic features of the decomposition of iron carbonyls on carriers is the intermediate formation of relatively stable subcarbonyl species. The main decarbonylation product is carbon monoxide.[33,34,42,43,50,57]

Further decarbonylation at higher temperatures leads to the irreversible decomposition of the subcarbonyl species with formation of oxidised or reduced forms of iron. Together with CO, H_2 and traces of hydrocarbons are evolved under these conditions. The formation of H_2 is explained by the interaction of zerovalent iron with the protons of the surface OH groups:[34,42,50,57]

$$2Z{-}OH + Fe^0 \rightarrow (Z{-}O^-)_2Fe^{2+} + H_2 .$$

From this it follows that the ratio of the oxidised and reduced forms of iron in the deposited iron carbonyl catalyst is determined mainly by the nature of the carrier, i.e. by the properties of the surface OH groups, and also by the ratio of these groups and the active component.

The decomposition of iron carbonyls on the HY zeolite leads to the oxidation of iron to Fe^{2+}, while the NaY zeolite mainly stabilises iron in the zerovalent state.[35,36,42] Graphite has no surface OH groups and the oxidation of iron is therefore not observed on decomposition of $Fe(CO)_5$ on this carrier.[57] It has been shown that, with increase in the MgO dehydration temperature, the fraction of reduced forms of iron increases.[40,41,46] The authors explain this by the decrease in the concentration of surface OH groups during the preliminary heat treatment.

A decrease in the concentration of surface OH groups is also caused by the treatment of Al_2O_3 with potassium hydroxide.[58] It has been shown[54,55] that an increase in the fraction of the reduced forms of iron in the catalyst obtained with increase in the potassium content is observed in the decomposition of iron carbonyls deposited on Al_2O_3 subjected to a preliminary treatment with KOH.

We shall consider the available few data concerning the influence of the nature of the carrier on the degree of dispersion of the catalyst formed. Iron particles 40–50 Å in size have been obtained in the decomposition of the same iron carbonyl complex on Al_2O_3 and particles 140 Å in size have been obtained on SiO_2.[47] Particles of the active component 20–90 Å in size have been detected after the decomposition of iron carbonyls on Al_2O_3 [33] and MgO.[40] It has been established that catalysts containing more highly dispersed particles are formed on decomposition of $Fe(CO)_5$ on Al_2O_3 than in the reaction using $Fe_3(CO)_{12}$.[50,51] An increase

in the decomposition temperature of the carbonyl complexes decreases the degree of dispersion of the iron particles obtained on Al_2O_3 or graphite.[50,51,57] The synthesis of hydrocarbons from CO and H_2 on an iron carbonyl catalyst has a considerable effect on the degree of dispersion of the iron particles. After such synthesis at 270 °C at atmospheric pressure, the size of the iron particles obtained by decomposing $Fe(CO)_5$ on Al_2O_3 increased by a factor of 10–25 (to 200–500 Å).[33]

Thus the degree of dispersion of the active component in the catalyst obtained by decomosing iron carbonyls on carriers depends on a series of parameters (the conditions in the decomposition of the carbonyl complexes, the nature of these complexes, and the properties of the carrier). At the same time we may note that the carbonyl systems are characterised by a higher degree of dispersion, which is a general feature of distinguishing them from the deposited catalysts obtained from inorganic iron compounds.[53]

3. Ruthenium and Osmium Carbonyls

The ruthenium and osmium carbonyl complexes frequently manifest common properties in their interaction with the surfaces of oxide carriers and also on heat treatment[59–87] (Table 3). These systems have been investigated by the IR,[44,59–68,71–85,87] UV,[65,79] and EPR spectroscopy[86] and by the thermoprogrammed decomposition method.[44,59,64,73,77]

Table 3. The state of the metal in the thermal decomposition of ruthenium and osmium carbonyls on different carriers.

Initial carbonyl	Carrier	T, °C	State of the metal
$Ru_3(CO)_{12}$*	Al_2O_3 (Refs.59-65), SiO_2 (Refs.44, 59, 61-63, 65, 66) MgO (Ref.60), TiO_2 (Ref.61), NaY zeolite (Refs.62, 63)	25–100	$[HRu_3(CO)_{10}]$ $(OM\lessgtr)$ or cluster Ru carbonyls
	Al_2O_3 (Refs.59, 61, 64, 65, 67), SiO_2 (Ref.61), TiO_2 (Ref.61)	~100	$Ru^{II}(CO)_2(OM\lessgtr)_2$
	Al_2O_3 (Refs.59-64, 65, 67-72), SiO_2 (Refs.44, 59, 61-63, 65, 66), TiO_2 (Ref.61), NaY zeolite (Refs.62, 63)	>100	Ru^0, Ru (ox.)
$Os_3(CO)_{12}$**	Al_2O_3 (Refs.73-83), SiO_2 (Refs,71, 73-75, 80), MgO (Refs.84, 85), TiO_2 (Refs.73-75, 80), ZnO (Ref.75)	25–100	$[HOs_3(CO)_{10}]$ $(OM\lessgtr)$ or cluster Os carbonyls
	Al_2O_3 (Refs.75-77, 81, 83, 86), SiO_2 (Refs.71, 75), MgO (Ref.85), TiO_2 (Ref.73), ZnO (Ref.75)	200–400	$Os^{II}(CO)_2(OM\lessgtr)_2$
	Al_2O_3 SiO_2 (Refs.73, 74, 79, 80), TiO_2 (Refs.73, 74, 80)	200–300	Os_{12} carbonyl clusters
	Al_2O_3 (Refs.81, 87)	300	Os^0, Os (ox.)

*In Refs.59 and 60, the initial carbonyl was $H_4Ru_4(CO)_{12}$.
**In Refs.71, 73, and 74, the initial carbonyl was $Os_6(CO)_{18}$.

At temperatures up to 100 °C, the ruthenium clusters retain their structure on the surfaces of certain inorganic carriers. However, on SiO_2 and Al_2O_3 they acquire a structure of the type $[HRu_3(CO)_{10}](OM\lessgtr)$.[59,61,66] A structure of type (IV) is obtained on the more basic MgO carrier.[60]

It has been shown[59] that the amount of $Ru_3(CO)_{12}$ chemisorbed on Al_2O_3 is proportional to the concentration of surface OH groups, which depends in its turn on the temperature of the preliminary treatment of the carrier.

At higher temperatures, partial decarbonylation of the surface complexes with formation of stable subcarbonyl species, apparently of the cluster type, is observed on Al_2O_3. Such species have not been detected[59] on SiO_2 but it has been established[61] that subcarbonyls are formed. The oxidation state of ruthenium in such surface complexes, formed on Al_2O_3 and SiO_2, changes from 0 to +4.[59,61,64–68] The cluster $[Ru_6C(CO)_{16}]^{2-}$ is formed on MgO.[60]

Above 100 °C, the subcarbonyl decomposes with formation of oxidised or reduced forms of ruthenium.[72] It is noteworthy that this process is reversible—treatment of the catalysts with CO at 200 °C regenerates the initial subcarbonyl, which apparently indicates a high degree of dispersion of ruthenium on the carrier surface and possibly the retention of the cluster structure of the "residues" of the complex.[59,61,69] It has been established[64,67,68] that, on decomposition *in vacuo* of the ruthenium carbonyls deposited on Al_2O_3, ruthenium produces less reduced but more highly dispersed particles than on decomposition of the above carbonyls in an H_2 atmosphere.

The degree of dispersion of ruthenium in the catalysts obtained has been determined[63,66,69,70] from the degree of adsorption of H_2 or CO. It has been shown[69,70] that the degree of dispersion of the catalyst obtained by decomposing $Ru_3(CO)_{12}$ on Al_2O_3 is four times higher than for the analogous sytems based on $RuCl_3$. Particles 20–40 Å in size have been detected on the surfaces of the latter. The size of the ruthenium crystallites obtained as a result of the decomposition of $Ru_3(CO)_{12}$ on Al_2O_3,[69] SiO_2,[66] and the NaY zeolite[63] does not exceed 10–14 Å.

The structure of the surface complexes formed as a result of the adsorption of $Os_3(CO)_{12}$ on carriers is the same as for the surface ruthenium carbonyls.[71,75–77] However, the deposited osmium carbonyls are more stable and their decomposition requires higher temperatures. At the present time there is no single view concerning the structure of osmium subcarbonyls on the Al_2O_3, SiO_2, MgO, and TiO_2 surfaces. It has been suggested[71,75–77,81,83,85] that mononuclear species of the type $Os^{II}(CO)_{2-3}$(ads.) are stabilised on the carrier surface. On the other hand, it has been concluded[73,74,79,80,84] that the subcarbonyls formed have a cluster structure and that they incorporate up to 12 osmium atoms. Such differences have been explained[73] by the different preliminary types of treatment of the carrier. It has been suggested that osmium carbonyl clusters are stabilised on carriers dehydrated to a high degree and that a high concentration of surface OH groups leads to the dissociation of the Os–Os bonds and the formation of mononuclear species. Further studies are necessary in order to establish reliably the structure of the subcarbonyl species and also the factors which determine the latter.

Osmium subcarbonyls on the Al_2O_3, SiO_2, TiO_2, and MgO surfaces are distinguished by a high stability and do not decompose *in vacuo*, in an inert gas atmosphere, or in an atmosphere consisting of a mixture of CO and H_2 even at 300–400 °C.[75,76,84–86] However, the formation of metallic osmium has been observed after the treatment of the catalyst in an H_2 atmosphere at 300 °C.[81]

It has been suggested[75,84–87] that the degree of dispersion of osmium in the catalysts investigated is very high and that its distribution is close to being molecular.

Having compared the ways in which iron, ruthenium, and osmium carbonyls interact with the surfaces of inorganic carriers, one may conclude that the formation of surface carbonyl complexes with a cluster structure is characteristic of all these systems. Their thermal stability increases in the sequence Fe < Ru < Os. In certain cases,[75,82,84] surface

osmium carbonyls are detected in the catalyst after the synthesis from CO and H_2 at atmospheric pressure and temperatures in the range 300–400 °C.

4. The Carbonyls of Other Group VIII Metals

The interaction of cobalt, rhodium, and iridium carbonyls with inorganic carriers has been little studied. It has been demonstrated by IR spectroscopy that tetranuclear cluster carbonyls are formed on the Al_2O_3, SiO_2,[88–92] MgO, TiO_2, and ZrO_2 [90] surfaces, The structures of these complexes apparently correspond to structure (III). On the other hand, it has been found that[93] $Co_3(CO)_9CH_3$ disproportionates on the surfaces of Al_2O_3, SiO_2, or the NaY zeolite with formation of Co^{2+} and $[Co(CO)_4]^-$ and that the carriers can be arranged in the following sequence in terms of the rate of this reaction: $Al_2O_3 > NaY > SiO_2$.

The study of the thermoprogrammed decomposition of cobalt carbonyl complexes on Al_2O_3 and SiO_2 showed[88,89,91] that, up to 100–150 °C, the relatively stable subcarbonyl complexes exist on the surface. At higher temperatures these species decompose irreversibly with formation of metallic cobalt and its oxidised forms.[89–92,94,95]

The degree of dispersion of the active component on the carrier surface depends on the conditions in the preparation of the catalyst and also on the nature of the carrier. An increase in the rates of temperature rise during the decomposition of surface carbonyl complexes leads to the formation of more dispersed catalysts.[92,94] The cobalt particles size on SiO_2 is greater than on Al_2O_3 and TiO_2. In certain cases it is possible to obtain systems containing cobalt crystallites 20–50 Å in size.[92] The lower degree of dispersion of the Co/SiO_2 catalysts has been explained[92] by the weak bond between the carbonyl complexes and the surface. Modification of the SiO_2 surface by titanium hydride complexes promotes the growth of the degree of dispersion of the metal in the cobalt catalysts.[96]

As in the case of cobalt carbonyls, the interaction of rhodium carbonyls with the SiO_2 surface does not alter the structure of the initial complexes.[97–99] On the other hand, the adsorption of $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, or $[Rh(CO)_2Cl]_2$ on Al_2O_3 from the gas phase or an organic solvent followed by treatment with CO leads to the formation of only the one complex $Rh_6(CO)_{16}$ on the surface.[97,99,100] In the interaction of $Rh_6(CO)_{16}$ with Al_2O_3 or MgO, the surface mononuclear carbonyl $Rh^I(CO)_2$ (OM–) (here M = Al or Mg) was identified by IR spectroscopy.[101,102]

At 100–200 °C *in vacuo* or in an H_2 atmosphere, the surface rhodium carbonyls decompose with formation of metal crystallites[100,103,104] whose size is close to 10 Å.[103] In the course of the decomposition of rhodium carbonyls on carriers, the intermediate formation of subcarbonyl surface complexes was discovered.[95,98,102,104,105] In contrast to pure H_2, in the presence of a mixture of CO and H_2, the surface carbonyl complexes are present together with metallic rhodium on the ZnO surface even at 400 °C.[104]

The interaction of $Ir_4(CO)_{12}$ with Al_2O_3 and SiO_2 has been investigated[106,107] by IR spectroscopy. At 20–100 °C the carbonyl is physically adsorbed on the carrier surface, to a lesser extent on SiO_2 than on Al_2O_3. Iridium carbonyl decomposes on carriers *in vacuo* at 100–200 °C with the intermediate formation of subcarbonyl mononuclear species of the type of $Ir(CO)_2$(ads.).[107] On raising the temperature to 300 °C, the surface iridium complexes are converted irreversibly into metallic iridium. Oxidised forms of iridium are then also formed on Al_2O_3 under these conditions and are reduced to the metal on treatment with H_2 at 300 °C.[108,109] According to Anderson and Howe,[108] the size of the iridium crystallites is approximately 10 Å, while Tanaka et al.[109] state that species incorporating about 20 iridium atoms are formed.

It has been established by IR spectroscopy that a complex of the type $Ni(CO)_nL_{4-n}$ (n = 2, 3; L = Ph_3P or Al_2O_3) is formed at room temperature as a result of the adsorption of $Ni(CO)_4$ on Al_2O_3 containing Ph_3P.[110] The decomposition of $Ni(CO)_4$ adsorbed on Al_2O_3, HY and NaY zeolites,[111] and NaX and CaX zeolites,[112,113] has been investigated. The size of the metallic nickel crystallites is 500–2000 Å on Al_2O_3 [111] and less than 30 Å on type X zeolites.[113] The decomposition of the carbonyl on zeolites proceeds with the intermediate formation of subcarbonyl complexes with the ratio Ni : CO = 1. It has been suggested[113] that the nickel crystallites are localised within the zeolite cavities and that this prevents the aggregation of the highly dispersed particles.

Highly dispersed platinum catalysts with metallic platinum particle size less than 10 Å have been obtained by decomposing the complexes $[NEt_4][Pt_3(CO)_6]_n$ (n = 1–5) deposited on SiO_2 or Al_2O_3.[114] The carbonyl complexes were decomposed at 160–250 °C *in vacuo* or in an H_2 atmosphere.

The interactions of heterometallic carbonyl clusters with inorganic carriers have been studied in a number of investigations[115–124] in order to obtain highly dispersed bimetallic particles on their surfaces. It has been shown[115] that the interaction of the $H_2RuOs_3(CO)_{13}$ cluster with Al_2O_3 in an atmosphere of CO and H_2 at 100–200 °C results in the formation of the $[H_3RuOs_3(CO)_{12}]^-$ anion on this surface. On the other hand, $H_3FeOs_3(CO)_{13}$ on SiO_2 decomposes at 130 °C in argon, forming metallic iron and $HOs_3(CO)_{10}(O–Si\equiv)$.[116] The osmium cluster formed is fully decarbonylated at temperatures above 250 °C with formation of metallic osmium, whose particle size is about 16 Å.[116]

It has been suggested that the decomposition of $Co_2Rh_2.(CO)_{12}$ and $Co_3Rh(CO)_{12}$ on ZnO [105,117] and $Co_2Rh_2(CO)_{12}$ on SiO_2 [118] leads to the formation of highly dispersed bimetallic particles. It has been shown[119] that the decomposition of $Co_2Rh_2(CO)_{12}$ or $Co_3Rh(CO)_{12}$ on Al_2O_3 at 400 °C in hydrogen makes it possible to obtain bimetallic clusters in which the ratio of the metals remains approximately the same as in the initial carbonyl complexes. Catalysts of analogous composition, obtained by the deposition of the salts $RhCl_3$ and $CoCl_2$, are much less dispersed.[119]

Bimetallic catalysts containing particles 15–30 Å in size have been obtained from $H_2RhOs(CO)_{10}$(acac) and $H_2FeOs_3.(CO)_{12}$ using Al_2O_3 as the carrier.[120]

The decomposition of the carbonyls $Fe_nRu_{3-n}(CO)_{12}$ (n = 1–3) on charcoal leads to the formation of Fe–Ru crystallites whose surface is enriched in iron.[121] The use, instead of the bimetallic cluster, of a mixture of $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ having the same composition altered appreciably the properties of the catalysts.

A similar study of the properties of catalysts obtained by decomposing $Ru_3(CO)_{12}$ on a reduced Pd/SiO_2 catalyst[122–124] showed that at room temperature the carbonyl is adsorbed on the surface and is then partly oxidised. The subsequent reduction of the catalyst with hydrogen leads to the formation of bimetallic Ru–Pd particles whose size is less than 16 Å.

Thus, catalysts containing the reduced metals can be obtained by decomposing transition metal carbonyls on inorganic carriers. It is noteworthy that the decomposition conditions and also the nature of the carbonyl and the carrier influence significantly this process. During the decomposition of almost all metal carbonyls, the formation of intermediates subcarbonyl complexes on the carrier surfaces was observed. At the present time the influence of various factors on the degree of dispersion of the active component in the catalyst obtained has not as yet been adequately elucidated. Nevertheless, there is no doubt that the catalysts

obtained from metal carbonyls are characterised by a higher degree of dispersion than those prepared from inorganic compounds. This is apparently caused by the mild preliminary treatment of the metal carbonyl catalyst. We may note that the metal-deposited systems, prepared by traditional methods, are usually reduced with hydrogen at high temperatures, which leads to the sintering of the metal into large crystallites.

III. SYNTHESIS OF ORGANIC COMPOUNDS FROM CO AND H_2 IN THE PRESENCE OF METAL CARBONYL CATALYSTS

As stated above, deposited metallic catalysts, obtained from metal carbonyls, are distinguished from traditional systems having the same composition by a higher degree of dispersion and a higher degree of reduction of the active component. In particular, metal carbonyl catalysts are therefore characterised by a higher specific activity in the synthesis of hydrocarbons or oxygen-containing compounds from CO and H_2.

The use of polymetallic carbonyl clusters makes it possible to obtain in a number of instances catalysts with unique properties, frequently exhibiting a high selectivity in many chemical reactions.

1. Molybdenum and Tungsten Catalysts

Molybdenum and tungsten carbonyl catalysts, deposited on Al_2O_3 and containing from 1% [20,23,24] to 3–5% [125,126] of molybdenum or tungsten, are used for syntheses from CO and H_2. The activity of the molybdenum catalysts is approximately 5 times greater.[23,24] Comparison of the molybdenum and tungsten carbonyl catalysts with traditional systems of analogous composition has shown that the latter are less active. This has been attributed to the higher degrees of reduction and the greater degree of dispersion of the active component in the carbonyl systems.[23,24,125,126] Preliminary treatment of the carrier before the adsorption of the carbonyl has an appreciable influence on the activity of the molybdenum carbonyl catalyst. In a flow system at atmospheric pressure at 300 °C, the activity of the catalysts based on Al_2O_3 heat-treated at 950 °C is 0.04 mol CH_4 (g-atom Mo)$^{-1}$ s^{-1}, while that for Al_2O_3 heated at 500 °C is 0.001 mol CH_3 (g-atom Mo)$^{-1}$ s^{-1},[23,24] which is apparently due to the lower degree of reduction of molybdenum in the latter case.

The principal products of the synthesis from CO and H_2 in the presence of molybdenum carbonyl complexes at atmospheric pressure are CH_4 and CO_2. Together with the latter, C_2H_6 and C_3H_8 are formed in much smaller amounts.[23,24] A mixture of C_1–C_6 hydrocarbons, with CH_4 and C_2H_6 predominating, has been obtained from CO and H_2 at 25 atm, 350 °C, and a volume flow rate of 1300 h^{-1}.[125] Promotion of the molybdenum carbonyl catalyst with 4% of potassium lowers the activity and increases the fraction of olefins in the synthesis product, whose content does not, however, exceed several per cent.[125] The activity and selectivity of the catalyst remained unchanged during 5–20 h of their use.[23,24,125] A mixture of C_1–C_4 hydrocarbons, with the contents of CH_4 (60%) and C_2H_6 (25%) predominating, has been obtained from CO and H_2 at 350 °C and 25 atm in the presence of a tungsten carbonyl complex based on Al_2O_3.[126]

2. Iron Catalysts

The considerable interest shown by investigators in iron carbonyl catalysts is due to the high selectivity of these systems in the synthesis of light olefins from CO and H_2 and also by the ready availability and low cost of $Fe(CO)_5$. Unfortunately, comparison of the results obtained by different authors is not always possible because different methods are used even for synthesis of catalysts having the same composition. This also applies to the methods of synthesis from CO and H_2.

Iron carbonyl catalysts based on Al_2O_3, SiO_2, MgO, La_2O_3, and MnO exhibit a high selectivity in the synthesis of light olefins from CO and H_2, whose yield can exceed 50% at 170 to 300 °C and 1–10 atm.[33,40,127–129] The greatest fraction is that of C_3H_6, which falls somewhat under the conditions where the catalyst has been used for a long time.[33] At the same time a decrease of the degree of dispersion of the catalyst is observed. On these grounds, the authors[33] concluded that light olefins are synthesised from CO and H_2 on highly dispersed particles of the active component of the catalyst.

At 250 °C, the highest activity is shown by catalysts based on MgO, while those incorporating Al_2O_3, SiO_2, TiO_2, and ZrO_2 are less effective.[130] The composition of the synthesis products in the presence of all these systems is approximately the same. Thus the CH_4 content is 27–37%, while the proportion of olefins in the C_2–C_3 fraction is 72–96%.[130]

The physicochemical and catalytic properties of systems obtained by decomposing potassium carbonyl ferrates on Al_2O_3 and SiO_2 have been studied in detail.[47] A mixture of C_1 and C_6 hydrocarbons, whose olefin content exceeds 50%, is formed in the presence of these systems from CO and H_2 at 270 °C and atmospheric pressure. The degree of conversion of CO was 2–7% on the Al_2O_3-based catalyst and 0.2% on the SiO_2-based catalyst. Catalysts of analogous composition, prepared using inorganic compounds (salts) of iron and potassium, show an activity smaller by a factor of 40–50.[47] The change in the atomic ratio K : Fe in the carbonyl catalysts from 2 to 1 for an overall iron content of 3% tends to increase the activity by a factor greater than 3 with the simultaneous diminution of the yield of olefins and C_5–C_6 hydrocarbons and an appreciable decrease in the activation energies for the methane formation and conversion reactions of CO.[47]

The influence of the conditions of the synthesis from CO and H_2 and also of the composition of the Fe/Al_2O_3 carbonyl catalysts promoted with potassium on its activity and selectivity has been investigated.[45,49,55,131,132] Comparison of the catalysts obtained from $Fe(CO)_5$ [49,132] and $Fe_3(CO)_{12}$ [45,131] showed that, for the same iron and promoting agent contents, they exhibit identical properties in synthesis from CO and H_2. The main products of the synthesis in the presence of these systems at 350–450 °C were CH_4, C_2H_4, C_3H_6, and CO_2. The increase in the iron content in the catalyst from 0.15 to 1.8% for a constant content of the promoting agent (potassium) lowered the fraction of ethylene and propene in the products of the synthesis from 70 to 40% and increased the degree of conversion of CO from 4 to 20%.[132] The Fe–K–Al_2O_3 catalysts containing 7–8% of potassium exhibit the highest activity.[131,132] The increase in the activity of the Fe–K–carbonyl catalyst with increasing content of potassium in the latter has been attributed[55] to the decrease in the fraction of the oxidised form of iron formed on decomposition of the initial carbonyl complexes. The increase in the selectivity of the Fe–K–Al_2O_3 catalyst in the formation of ethylene and propene is favoured by a decrease in the temperature of the synthesis (from 450° to 350 °C), by a decrease in the H_2 : CO ratio (from 4 : 1 to 1 : 3), and also by an increase in the volume flow rate of CO and H_2 (from 15 to 100 h^{-1}).[131]

Type Y zeolites can be used as carriers for iron carbonyl catalysts,[37,42,133] The main products of the synthesis from CO and H_2 under static conditions in the presence of iron catalysts containing the HY, NaY, and CaY zeolites at 1–20 atm and 250–400 °C were C_1–C_4 alkanes and also CO_2.[37,42]

The increase in the iron content from 3 to 8% led to an appreciable growth of the activity of these systems.[37] Mixtures of C_1–C_4 hydrocarbons containing up to 30% of ethylene and propene have been obtained in a flow system in the presence of iron carbonyl catalysts containing the BeY, MgY, CaY, SrY, and BaY zeolites at 1 atm and temperatures in the range 300–400 °C.[133] In terms of their activity in the synthesis of hydrocarbons from CO and H_2, the above catalyst can be arranged in the sequence BaY > SrY > CaY > MgY > BeY. It is the same as the sequence based on the increase in the acid properties of the carriers—type Y zeolites.[133]

Iron carbonyl catalysts of the synthesis of hydrocarbons from CO and H_2 can undoubtedly be of practical value. Analysis of patent literature[48,134–137] shows that effective catalytic systems, based on deposited iron carbonyls and permitting the synthesis of lower olefins from CO and H_2 with a high selectivity, have now been created.

3. Ruthenium and Osmium Catalysts

The properties of ruthenium and osmium carbonyl catalysts in syntheses from CO and H_2 depend greatly on the experimental conditions. As stated above, at temperatures up to 200 °C, these systems are reversibly decarbonylated. Thus, when the synthesis is carried out in the above temperature range, the catalyst surface contains, together with the oxidised and reduced forms of the active component, also cluster carbonyl complexes, which has a definite influence on the activity and selectivity of the above systems.

It has been shown[33,47,48,60] that at 200 °C and 1–20 atm the activity of the ruthenium carbonyl catalyst containing Al_2O_3 is higher than that of traditional systems. At the same time the composition of the hydrocarbons obtained (C_1–C_5) differs insignificantly from that of the product of synthesis in the presence of catalysts prepared from inorganic ruthenium compounds. When ruthenium carbonyls are deposited on MgO, the ruthenium carbonyl cluster persists on the catalyst surface during the synthesis from CO and H_2 and it has been possible to isolate it after the synthesis and to identify as $[Ru_6C(CO)_{16}]^{2-}$.[60] A distinctive feature of such systems is their lower activity and also the high content of olefins in the hydrocarbon mixtures formed (23–28%). At the same time up to 21–27% of C_1–C_2 alcohols are formed.[60] A mixture of C_1–C_6 hydrocarbons containing up to 80% of olefins has been obtained from CO and H_2 at 200 °C and 500 mmHg in the presence of the $Ru_3(CO)_{12}/Al_2O_3$ catalyst.[70] Promotion of the ruthenium carbonyl catalyst with potassium lowers its activity and increases its selectivity in relation to the formation of olefins. The introduction of boron or phosphorus into the catalyst produces the opposite results.[138] The $Ru_3(CO)_{12}/CeO_2$ catalyst, in the presence of which a mixture of hydrocarbons containing 35% of C_2–C_4 olefins was obtained from CO and H_2, has been proposed.[139]

Catalysts active in the synthesis of C_1–C_5 hydrocarbons at 270 °C have been obtained using $Na[HRu_3(CO)_{11}]$. In terms of their activity, these catalysts on different carriers can be arranged in the following sequence of the latter Al_2O_3 > SiO_2 > MgO > TiO_2. Catalysts containing TiO_2 and MgO are the most selective in the formation of ethylene and propene.[140]

At temperatures of about 300 °C and above, methane is formed as the main product from CO and H_2 in the pesence of ruthenium carbonyl catalysts containing SiO_2,[128,141] Al_2O_3, or the NaY zeolite.[141] Methane is also produced selectively from mixtures of CO_2 and H_2 in the presence of the above ruthenium carbonyl systems.

Catalysts obtained by adsorbing $Ru_3(CO)_{12}$ on type NaX, NaY, KL, and NaM zeolites and also SiO_2 have been investigated.[142,143] The metal content in the catalyst was from 0.4 to 1.4%. In terms of their specific activity, the catalysts on different carriers can be arranged in the sequence NaY > NaX > NaM > KL, SiO_2.[142] The activation energy for the conversion of CO in the presence of these catalysts is about 23 kcal mol^{-1}. At 250 °C and 1 atm, the main products of the synthesis were C_1–C_5 hydrocarbons. The $Ru_3(CO)_{12}$/NaY catalysts proved to be the most selective as regards the formation of olefins and made it possible to obtain up to 45% of C_2–C_4 olefins under the conditions indicated. The increase in the temperature of the synthesis from 200° to 340 °C increases the fraction of methane and reduces the olefin/paraffin ratio in the synthesis products.[142] A ruthenium carbonyl catalyst on the HM zeolite has been proposed for the synthesis of C_1–C_7 hydrocarbons, including up to 69% of C_4–C_5 hydrocarbons, from CO and H_2.[144]

There have been only a few studies of the catalytic properties of osmium carbonyl catalysts.[33,80–82,84,87] In particular, the kinetics of the conversion of CO and CO_2 into methane at 180–400 °C has been studied.[80] In terms of their activity these catalysts can be arranged in the sequence SiO_2 > TiO_2 > Al_2O_3 as a function of the carriers used.[80] A mixture of C_1–C_4 hydrocarbons has been obtained in the presence of osmium catalysts based on SiO_2 at 200 °C [33] or on MgO at 300 °C.[84] As for the ruthenium systems, the osmium carbonyl catalysts containing the active component in the metallic state are more active than the catalysts on the surfaces of which the carbonyl complexes are present.[81,82] The introduction of potassium into the osmium carbonyl catalysts[82] increases their selectivity in relation to the formation of olefins.

It has been shown[87] that osmium catalysts based on Al_2O_3 are active in the synthesis of C_1–C_7 alkanes at 250–300 °C and 10 atm. Their activity increases with decrease in the degree of dispersion of the metallic osmium. It has been suggested[87] that the active centres for the synthesis of alkanes are metallic osmium clusters and those for the synthesis of oxygen-containing compounds are carbonyl complexes on the catalyst surface.

4. Cobalt Catalysts

In the presence of cobalt carbonyl catalysts, the main products of the synthesis from CO and H_2 are saturated hydrocarbons with a normal structure. It has been shown[145–147] that the pore diameter in the carrier (Al_2O_3, aluminosilicate) influences decisively the process selectivity: a decreases in the pore diameter shifts the selectivity maximum towards the formation of lighter hydrocarbons without altering the catalyst activity. For example, the main products of the synthesis in the presence of the 2% CO/Al_2O_3 catalyst at 200 °C and with an average carrier pore diameter of 300 nm are C_{14}–C_{20} alkanes, while for an average pore diameter of 6.5 nm the main products are C_4–C_9 alkanes.[147] The authors[147] explain this phenomenon by selective condensation (as a function of the molecular weight) within the catalyst pores of the hydrocarbons formed during the synthesis with their subsequent hydrogenolysis to lighter hydrocarbons. However, these features are valid only for systems in which almost the entire cobalt is present in the catalyst pores, i.e. for catalysts containing small amounts of cobalt (several per cent).

The influence of the nature of the carrier and also of the conditions in the preparation of the cobalt carbonyl catalyst (1–4% CO) on its properties in the synthesis of hydrocarbons for CO and H_2 has been studied in detail.[90–92,94,148–152] It has been shown that,[92,94] when the temperature is raised rapidly in the decomposition of carbonyl complexes, the latter break down with formation of highly dispersed metallic particles on the SiO_2, Al_2O_3, and TiO_2 surfaces. These

catalysts exhibit an activity exceeding by a factor of 2–10 the activity of systems based on inorganic cobalt compounds. If the decomposition is carried out with a slow temperature rise (~1 K min^{-1}), less dispersed catalysts are formed and exhibit a low activity in the synthesis of organic compounds from CO and H_2. The main products of the synthesis using cobalt catalysts on Al_2O_3, MgO, SiO_2, TiO_2, and ZrO_2 containing 1–24% CO are, at 160–180 °C, C_4–C_{22} hydrocarbons with the normal structure.[148] It has been suggested that[148] in this instance α-olefins are intermediates in the synthesis of the alkanes. In terms of their activity the above catalysts can be arranged in the following sequence based on the nature of the carrier: $SiO_2 > TiO_2 > ZrO_2 \geq Al_2O_3 > MgO$.[92]

Cobalt catalysts on TiO_2 and ZrO_2 manifest a high selectivity in relation to the formation of higher molecular weight hydrocarbon fractions.[92,149] An increase in the surface concentration of cobalt and also preliminary partial oxidation of the catalyst with air shift the selectivity maximum towards the formation of heavier hydrocarbons.[149] It is noteworthy that, in the presence of the Co/MgO and Co/Al_2O_3 catalysts, up to 25% of alcohols is formed together with hydrocarbons.[148] It has been concluded[96] that an increase in the degree of dispersion of cobalt lowers the specific activity of the catalyst and increases the fraction of light hydrocarbons as well as oxygen-containing compounds in the synthesis products.

The synthesis of hydrocarbons from CO and H_2 in the presence of cobalt carbonyl catalysts (5–15% Co) has been investigated.[91,150,152] The main products of the synthesis at 180–200 °C and atmospheric pressure were C_5–C_{22} hydrocarbons. The properties of the catalyst were estimated from the yields of the liquid hydrocarbons (B_L) per nm^3 of the mixture with the volume ratio $CO:H_2 = 1:2$ at a volume flow rate of 100 h^{-1}. In the absence of promoting agents, $B_L = 42$ nm^{-3} for the catalyst with 5–7% Co on Al_2O_3 and 28–34 g nm^{-3} for the catalyst with the same metal content on SiO_2.[150–152] Promotion of Co/SiO_2 by metal oxides (MgO, NiO, ZrO_2, and CoO) increases B_L.[151] Thus the introduction of up to 30% of CoO into the 7% Co/SiO_2 catalyst induces a sharp increase in B_L to 83 g nm^{-3}.[151,152] When a high-silica zeolite of the pentasil type is used as the carrier ($SiO_2:Al_2O_3 = 42$), the yields of liquid hydrocarbons are low, but the composition of the synthesis product differs appreciably from that obtained in the presence of the Co/Al_2O_3 or Co/SiO_2 catalysts.[152] The paraffins formed in the presence of the Co-zeolitic catalyst consisted mainly of C_5–C_{14} hydrocarbons and their content of isoalkanes reached 44%. A characteristic feature of these catalysts is also the presence in the synthesis products of small amounts of aromatic hydrocarbons.[152] The properties of cobalt carbonyl catalysts on SiO_2 and Al_2O_3 are appreciably influenced by the conditions in their preliminary treatment and by the gas employed in this process (CO, CO + H_2, Ar). Preliminary treatment of the catalyst with a mixture of CO and H_2 at 150 °C proved to be optimal.[91]

The kinetics of the synthesis of C_1–C_5 hydrocarbons from CO and H_2 in the presence of cobalt carbonyl catalysts (1.2–1.9% Co) has been investigated.[153] At 220 °C and for the ratio $CO:H_2 = 1:3$, the rates of reaction were 2.5×10^{-4} mol CO (g-atom Co)$^{-1}$ s^{-1} in the presence of Co/Al_2O_3 and Co/ZrO_2 and 4.4×10^{-4} mol CO (g-atom Co)$^{-1}$ s^{-1} in the presence of Co/SiO_2.

The activity of the cobalt carbonyl catalyst depends on the structure of the initial cobalt cluster. The catalyst obtained by depositing $Ph_2C_2Co_4(CO)_{12}$ on Al_2O_3 is the most active.[154] It has been established that the catalyst obtained by decomposing $Co_2(CO)_8$ or $Co_4(CO)_{12}$ on SiO_2 fully converts the $CO:H_2 = 1:2$ mixture into methane and CO_2 at 300–450 °C and a volume flow rate of 500 h^{-1}. A highly active cobalt catalyst promoted with palladium or platinum has been proposed for the synthsis of hydrocarbons.[155]

5. Rhodium, Iridium, and Platinum Catalysts

A distinctive feature of deposited rhodium, iridium, and platinum carbonyl catalyst is their high selectivity in relation to the formation of methanol and ethanol from CO and H_2. The catalyst obtained from $Rh_4(CO)_{12}$ and ZnO, CaO, or MgO showed the greatest selectivity in relation to the formation of methanol (91–99%) at 200–220 °C and 1 atm.[156–158] Using TiO_2, ZrO_2, ThO_2, amd CeO_2 as carriers for the rhodium carbonyl catalyst, it is possible to direct the process selectivity towards the predominant formation of ethanol from CO and H_2. Rhodium systems on SiO_2 and Al_2O_3 catalyse the formation of C_1–C_4 hydrocarbons.[33,156–158] It has been suggested[156] that, with decrease in the basicity of the carrier and with increase in its acidity, the selectivity of the catalyst in relation to the formation of oxygen-containing compounds diminishes and that in relation to the formation of hydrocarbons increases. The kinetics of the synthesis of CH_4 and ethanol in the presence of rhodium catalysts has been studied.[153] At 220 °C and for the ratio $CO:H_2 = 1:3$, the rates of reaction were 1.2×10^{-4} (Rh/Al_2O_3), 2.2×10^{-3} (Rh/ZrO_2), and 4×10^{-5} mol CO (g-atom Rh)$^{-1}$ s^{-1} (Rh/SiO_2). For the catalyst on ZrO_2, the rate of formation of methane under these conditions is 10 times greater than the rate of synthesis of ethanol. In the presence of catalytic systems on Al_2O_3 or SiO_2, mainly only hydrocarbons were formed from CO and H_2.[153]

The structure of the initial rhodium carbonyl cluster exerts a significant influence on the course of the synthesis in the presence of rhodium catalysts on La_2O_3.[156,158] Catalysts synthesised from $Rh_4(CO)_{12}$ and $Rh_6(CO)_{12}$ are the most active and selective in relation to the formation of alcohols. A method of synthesis of ethanol from CO and H_2 at 250 °C and 25 atm in the presence of the $Rh_6(CO)_{16}/ThO_2$ catalyst promoted with 1% Eu has been proposed.[159]

Iridium carbonyl catalysts on Al_2O_3 catalyse the formation of C_1–C_4 alkanes at 180–285 °C and 1 atm, the main product being CH_4 (72–78%).[33,47] On the other hand, the formation of methanol as well as methane was observed in the presence of the $Ir_4(CO)_{12}/ZnO$ catalyst.[157]

Catalysts based on cluster platinum carbonyls and ZnO or MgO are characterised by a high selectivity in relation to the formation of methanol (94–99%) at 170–260 °C and atmospheric pressure.[157]

6. Catalysts Based on Bimetallic Carbonyl Clusters

A promising trend in the synthesis of heterogeneous catalysts involves the use of bimetallic transition metal carbonyl clusters in the preparation of new catalytic systems. Polymetallic carbonyl clusters of almost all the Group VIII elements have now been synthesised.[160] The study of catalysts obtained by the thermal decomposition of bimetallic carbonyl clusters on the surfaces of inorganic carriers was initiated several years ago, but results demonstrating the promising nature of this procedure have already been obtained.

Catalysts obtained by decomposing the $H_2FeRu_3(CO)_{13}$ and $Fe_2Ru(CO)_{12}$ clusters and a mixture of $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ on SiO_2 have been tested in synthesis from CO and and H_2 at 250–280 °C and 1–19 atm.[128,161] The catalyst based on $H_2FeRu_3(CO)$, in the presence of which methane is mainly formed from CO and H_2, showed the highest activity. The catalyst based on $Fe_2Ru(CO)_{12}$ was less active but more

selective in relation to the formation of olefins. It is noteworthy that, when the Ru–Fe cluster was replaced by the equivalent mixture of $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$, the activity and selectivity of the specimen did not change. On the other hand, the opposite result has been described:[121] the replacement of catalysts obtained by decomposing $Fe_nRu_{3-n}.(CO)_{12}$ ($n = 0-2$) on charcoal by catalyst prepared from the mixture of $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ altered the catalytic properties of the system. The main products of the synthesis in the presence of these systems at 275 °C were C_1-C_4 alkanes.

Effective catalysts for the conversion of CO into methane have been obtained by decomposing the complex $H_2FeRu_3.(CO)_{13}$ on Al_2O_3, SiO_2, or the NaY zeolite.[141]

It has been shown[116] that, in terms of its activity and selectivity in the synthesis of C_1-C_4 hydrocarbons at 250 °C and 1 atm, the $H_2FeOs_3(CO)_{13}/SiO_2$ catalyst occupies an intermediate place between the $Fe_3(CO)_{12}/SiO_2$ and $Os_3(CO)_{12}/SiO_2$ catalysts.

The synthesis from CO and H_2 in the presence of the $H_2FeOs_3(CO)_{13}/Al_2O_3$ catalyst at 270 °C and 10 atm yielded CH_4 (49%), C_2H_6(11%), and $(CH_3)_2O$ (36%).[120] The $H_3CpNi.Os_3(CO)_9/Al_2O_3$ catalyst, active in the synthesis of CH_4 and C_2H_6 from CO and H_2 at 250–350 °C, has been described.[162]

The properties of the catalysts obtained by decomposing the cluster anion $[FeCO_3(CO)_{12}]^-$ depend greatly on the nature of the carrier. When aminated silica gel was used as the carrier,[163] a catalyst for the selective synthesis of light olefins from CO and H_2 at 240 °C and 1–40 atm was obtained. A characteristic feature of this catalytic system is the reduced content of olefins and the shift of the selectivity maximum towards light hydrocarbons with increase in pressure. On the other hand, the decomposition of $[FeCo_3(CO)_{12}]^-$ on SiO_2 promoted with titanium hydride complexes makes it possible to obtain a system which catalyses the formation of methanol (10%) and ethanol (30%) together with hydrocarbons at 180 °C and 1 atm.[164]

The introduction of platinum into the iron carbonyl catalyst greatly increases the activity with retention of a high selectivity in relation to the formation of light olefins.[165] The authors[165] suggest that, under the conditions of the preparation of the catalyst and the synthesis from CO and H_2, the platinum surface is partly coated by iron, which is responsible for the increase in activity.

The properties of catalysts based on $Co_2Rh_2(CO)_{12}$, $Co_3Rh(CO)_{12}$, $Co_4(CO)_{12}$, and $Rh_4(CO)_{12}$ on Al_2O_3, SiO_2, and ZrO_2 have been investigated.[153] At 200–220 °C and for the ratio $CO:H_2 = 1:3$, the main products of the synthesis were methane and ethanol. The bimetallic Co–Rh catalyst occupies an intermediate position between the cobalt and rhodium catalysts as regards activity. An increase in the Co:Rh ratio lowers the rate of conversion into methane and to a lesser extent, the rate of synthesis of ethanol. The maximum selectivity in relation to the formation of ethanol is reached for the ratio $Co:Rh = 1:1$.[153]

A comparative study of catalysts based on $Fe_3(CO)_{12}$ and $[NEt_4]_2[Fe_2Mn(CO)_{12}]$ on various carriers (Al_2O_3, SiO_2, MgO, TiO_2, and ZrO_2) has been carried out.[130] With the exception of the catalyst incorporating MgO, they all yield comparatively little methane and a large amount of heavy hydrocarbons in the synthesis. It is noteworthy that in this respect they differ from the catalysts of analogous composition obtained from iron and manganese nitrates. The authors[130] suggest that the Fe–Mn interaction takes place on the carrier surface also after the decomposition of the metallic cluster, in contrast to systems obtained by the decomposition of nitrates.

The Pd–Ru crystallites have been obtained[124] on the SiO_2 surface by adsorbing $Ru_3(CO)_{12}$ on the Pd/SiO_2 catalysts and by subsequent treatment with hydrogen. An increase in the Pd/Ru ratio drives the synthesis from CO and H_2 towards the preferential formation of methanol and the activity of the catalyst then passes through a minimum.

Thus the use of polymetallic carbonyl clusters for the preparation of catalysts constitutes a promising method of synthesis of highly dispersed catalysts. The fact that the additivity of the properties of the catalysts obtained by the separate deposition of the complexes is not observed in many instances, which indicates the possibility of the interaction of transition metals also after the decomposition of the carbonyl clusters, merits special attention.

IV. CONCLUSION

The synthesis of organic compounds from CO and H_2 is a complex and in most cases a multistage process incorporating consecutive and parallel reactions, the key stages of which are those involving the growth and termination of the hydrocarbon chain and also hydrogenation. The composition of the products of synthesis is influenced very strongly, together with the type of the catalyst employed, by the reaction conditions (temperature, pressure, volume flow rate, the ratio of CO and H_2, etc.). Therefore, as a consequence of the difference between the conditions and methods of synthesis, comparison of the results obtained in different studies in the presence of carbonyl catalytic systems having identical or similar compositions is not always possible.

This comparison is also hindered by two other factors. Different workers have used different carriers for the deposition of metal carbonyls and also different methods of deposition of the carbonyls and of the preliminary treatment of the catalyst. Furthermore, the methods employed to test the catalysts also differed: the contact time was varied from 1–2 h at a constant temperature to 5–20 days with a temperature rise. By analysing the above data, one can therefore achieve only the most general conclusions and comparisions.

Mainly metal carbonyl catalysts based on Group VI and VIII metals are active in the synthesis of light hydrocarbons and, in particular, of methane. In this case, the chain termination stage apparently predominates over the propagation stage. For example, the preferential formation of methane from CO and H_2 has been described for deposited molybdenum and tungsten,[20,23,24,125,126] iron,[37] ruthenium,[128,141] osmium,[33,80] cobalt,[141] rhodium,[153] and iridium catalysts.[33,47,157] The synthesis of C_1-C_4 hydrocarbons in the presence of iron,[37,42] ruthenium,[33,47,48,60,136,143,144] osmium,[81,82,84,87] cobalt,[153,154] and rhodium catalysts[33,156–158] has been described.

The ruthenium[60,70,136,138–140] and especially iron catalysts[33,40,45,47–49,55,127–137] are characterised by high selectivity in relation to the formation of lower olefins. These systems apparently possess a lower hydrogenating capacity, so that under the conditions of the synthesis the olefins formed initially are not hydrogenated to the corresponding alkanes. In the presence of these systems, there is no significant chain growth either.

Methanol and ethanol has been obtained only in the presence of rhodium[153,156–159] and iridium catalysts.[157]

High-molecular-weight hydrocarbons are formed from CO and H_2 only in the presence of cobalt systems,[90–92,94,96,145–152] which indicates the predominance of the hydrocarbon chain propagation stage over the termination stage in this instance.

Thus metal carbonyl catalytic systems for the specific synthesis of lower olefins, alcohols, or high-molecular-weight hydrocarbon from CO and H_2 have been most thoroughly developed and investigated. These catalysts can also be treated from a practical standpoint. The manufacture of iron and cobalt carbonyls has been achieved on an industrial

scale, which leads to prospects for the use of metal carbonyl systems based on them (with a low metal content) for the creation of stable and effective catalysts of synthesis from CO and H_2.

The fact that the systems are convenient for the investigation of the mechanisms of the syntheses of organic compounds from CO and H_2 and also of the influence of the composition and structure of the catalyst on its catalytic properties and for the elucidation of the nature and structure of the active centre for the synthesis is also fairly important.

Thus one may expect that in the future studies on the metal carbonyl catalysts of the synthesis of chemical products from CO and H_2 will continue.

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