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Super-pure Materials from Metal-organic Compounds

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Work on the preparation of super-pure materials by the decomposition of metal-organic compounds is reviewed. The decomposition methods, and the factors which influence the purity of the elements and compounds obtained, are discussed. The possible applications and the advantages of the thermal decomposition method are pointed out. 69 references.

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I. INTRODUCTION

The preparation of super-pure materials by using metal-organic compounds (MOC) has been intensively studied in recent years. In principle, the method is based on the decomposition of metal-organic compounds to elements or compounds whose purity is determined (depending on the experimental conditions) by the purity of the initial metal-organic compound.

The purification of substances such as metals, which are involatile and refractory by virtue of their atomic crystal lattice, has to be carried out at high temperatures and is therefore liable to cause contamination of the product by the material of the apparatus. On the other hand, the thermal decomposition of MOC (leading to the formation of elements or compounds) can be carried out at relatively low temperatures, with negligible contamination of the product by the material of the apparatus. Substances produced by thermal decomposition of MOC can be obtained either in the form of powders or as coatings on substrates of practically any composition and configuration.

Contamination with carbon is always a possibility in the preparation of pure substances by thermal decomposition of MOC, and therefore the use of volatile inorganic hydrides is preferred for the preparation of super-pure elements such as boron, germanium, phosphorus, tin, arsenic, antimony, etc.[1] However, volatile inorganic hydrides are known for only a few of the elements, and therefore the method has only a limited application. On the other hand, metal-organic compounds are known for practically all the elements; they can be synthesised by selective methods which already remove a number of impurities, and they can be intensively purified by fractional distillation, chromatography, or crystallisation. Furthermore, the carbon contamination of the product can be reduced (often to negligible proportions) by proper control of the thermal decomposition reaction and by suitable choice of the initial MOC.

In addition to their application in the preparation of highly pure substances by thermal decomposition, MOC are often used and purified on their own account. Organic derivatives of metals are very useful for the extraction of small amounts of one element from large amounts of

another element in order to concentrate the minor component or to purify the major component.

The aim of the present review is to collate the existing fund of experimental data on the preparation of pure substances from metal-organic compounds. We shall discuss the behaviour of trace impurities during the synthesis and purification of the MOC, and we shall analyse the effect of experimental conditions and of the type of MOC on the carbon contamination of the resulting elements and compounds. We shall stress the wide range of possible applications of the method, and the prospects of obtaining superpure substances from metal-organic compounds.

The review is confined to papers in which the purity of the initial metal-organic compounds and of the resulting elements and compounds is stated.

II. SELECTIVITY OF THE METHOD OF SYNTHESIS OF METAL-ORGANIC COMPOUNDS, AND PURIFICATION

In order to produce high-purity substances by thermal decomposition of metal-organic compounds we must have access to extremely pure MOC. The freedom of the resulting metals, alloys, and compounds from trace impurities of other elements is determined by the amount of these impurities present in the original metal-organic compound. Modern techniques of organic chemistry allow us to prepare metal-organic compounds of practically every element, and even to vary the type of compound produced from any one element, so that the scope of physicochemical methods of purification becomes much wider than in the corresponding inorganic systems. The most convenient and most widely used methods of purification of MOC are fractional distillation, chromatography, recrystallisation, and extraction. Zone melting, sublimation, molecular distillation, and other special methods can be used in particular cases.

One of the most important aspects of the preparation of super-pure substances by the decomposition of MOC is the tendency of the methods of synthesis to exclude originally present impurities. This is a consequence of the selectivity of the usual methods of synthesis. Thus, the preparation of alkyl derivatives of non-transition metals can be expected to yield a product in which the concentration of transition-metal impurities is lower than in the initial reagents, since transition metals do not readily form alkyl derivatives. A similar type of purification occurs also during the synthesis of organic transition-metal compounds, which tend to be purified from non-transition metal impurities.

Gribov and coworkers [2] have studied the behaviour of trace elements during the synthesis of non-transition MOC for the special case of the preparation of trimethylgallium from methyl iodide and a gallium-magnesium alloy:

$$Ga + Mg + CH_3I \rightarrow (CH_3)_3Ga + MgI_2$$

and other workers have reported similar studies of the preparation of the etherate of trimethylgallium by the Grignard reaction [3]

$$CH_3MgI + GaCl_3 \xrightarrow{(C_2H_5)_2O} (CH_3)_3Ga \cdot O(C_2H_5)_2,$$

and of bis-ethylbenzenechromium by Fischer's method [4].

The impurities in the initial gallium, chromium, and aluminium chlorides were probably present as chlorides and oxide chlorides, those in the metallic magnesium and aluminium were probably present as elements. Under the conditions used for the synthesis of these metal-organic compounds, impurities in the initial reagents could find their way into the final product as methyl, chloromethyl, oxide chloride, and arene compounds.

Table 2. Impurity content of bis-ethylbenzenechromium and of the starting reagents.

Substance	Impurity content, wt.%						
	Al	Mg	Mn	Si	Ni	Fe	Ti
$CrCl_3$	$>1\cdot10^{-2}$	$1\cdot10^{-2}$	$7\cdot10^{-3}$	$2\cdot10^{-2}$	$2\cdot10^{-3}$	$2\cdot10^{-3}$	$6\cdot10^{-3}$
$AlCl_3$	—	$1\cdot10^{-2}$	$3\cdot10^{-4}$	—	$4\cdot10^{-5}$	$>1\cdot10^{-2}$	$1\cdot10^{-3}$
Al	—	$>1\cdot10^{-2}$	$5\cdot10^{-3}$	—	$5\cdot10^{-3}$	$1\cdot10^{-2}$	$1\cdot10^{-2}$
$(EtC_6H_5)_2Cr$	$<1\cdot10^{-4}$	$3\cdot10^{-4}$	$3\cdot10^{-4}$	$<1\cdot10^{-3}$	$<1\cdot10^{-3}$	$<1\cdot10^{-3}$	$<1\cdot10^{-3}$

Analytical results for trace impurities in the initial reagents and in the final products (trimethylgallium etherate, trimethylgallium, and bis-ethylbenzene chromium) are summarised in Tables 1 and 2. It is evident that the impurity content is much lower in the MOC than in the starting materials. For example, the concentration of aluminium, magnesium, and silicon (which do not form the corresponding bis-arene compounds) is 1–2 orders of magnitude lower in bis-ethylbenzenechromium than in the starting materials. Trimethylgallium etherate and trimethylgallium contain 10–100 times less copper, magnesium, titanium, zinc, iron, nickel, aluminium, manganese, silver and silicon than the reagents used in their preparation (magnesium and gallium trichloride).

Table 1. Impurity content of trimethylgallium etherate, trimethylgallium, and starting reagents*.

Substance	Impurity content, wt.%												
	Cu	Mg	Zn	Al	Ti	Si	Sn	Pb	Cr	Mn	Fe	Ni	Ag
Mg tech.	$\geqslant5\cdot10^{-3}$	—	$>4\cdot10^{-2}$	$>1\cdot10^{-2}$	$1\cdot10^{-3}$	—	$1\cdot10^{-3}$	$>1\cdot10^{-2}$	$2\cdot10^{-3}$	$>5\cdot10^{-3}$	$1\cdot10^{-2}$	$2\cdot10^{-3}$	$5\cdot10^{-5}$
$GaCl_3$ tech.	$3\cdot10^{-4}$	$5\cdot10^{-4}$	$1\cdot10^{-3}$	$>1\cdot10^{-3}$	$1\cdot10^{-3}$	$6\cdot10^{-3}$	$1\cdot10^{-3}$	$>1\cdot10^{-3}$	$1\cdot10^{-3}$	$1\cdot10^{-4}$	$\geqslant1\cdot10^{-3}$	$5\cdot10^{-4}$	$5\cdot10^{-4}$
$(CH_3)_3Ga\cdot O(C_2H_5)_2$	$5\cdot10^{-5}$	$6\cdot10^{-5}$	$4\cdot10^{-4}$	$2\cdot10^{-4}$	$<1\cdot10^{-4}$	$2\cdot10^{-4}$	$4\cdot10^{-4}$	$4\cdot10^{-3}$	$<1\cdot10^{-3}$	$<1\cdot10^{-4}$	$4\cdot10^{-4}$	$1\cdot10^{-4}$	$<3\cdot10^{-5}$
Ga tech.	$3\cdot10^{-4}$	$1\cdot10^{-4}$	$2\cdot10^{-3}$	$1\cdot10^{-4}$	$<3\cdot10^{-3}$	$6\cdot10^{-3}$	$1\cdot10^{-4}$	$4\cdot10^{-3}$	$2\cdot10^{-3}$	$<5\cdot10^{-4}$	$6\cdot10^{-3}$	$5\cdot10^{-4}$	$4\cdot10^{-4}$
$(CH_3)_3Ga$ **	$6\cdot10^{-5}$	$5\cdot10^{-5}$	$2\cdot10^{-4}$	$1\cdot10^{-4}$	$<1\cdot10^{-4}$	$2\cdot10^{-4}$	$9\cdot10^{-5}$	$3\cdot10^{-4}$	$<4\cdot10^{-6}$	$2\cdot10^{-6}$	$9\cdot10^{-5}$	$5\cdot10^{-5}$	$<3\cdot10^{-6}$

*The tabulated values are the average of 3–5 determinations.

**Technical magnesium was used to prepare this material.

Trimethylgallium and its etherate are most effectively purified from those trace elements which do not form alkyl derivatives, and whose chlorides have a volatility very different from that of the gallium MOC. Even when the elements present as impurities in the starting materials can form the corresponding metal-organic compounds (zinc, tin, silicon) their concentration is significantly lower in the final MOC.

The behaviour of trace impurities in gallium chloride during the synthesis of gallium MOC has been studied by a radioactive tracer method[2] for the particular case of zinc. The isotope ^{65}Zn was added to gallium trichloride as zinc chloride, and the gallium trichloride was used to prepare trimethylgallium etherate. Only a very small fraction of the zinc present in the gallium trichloride was detected in the final trimethylgallium etherate: most of the radioactivity remained in the still residue left after distillation of the main product.

The selectivity of the methods of preparation of aluminium, tantalum, and niobium alkoxides has been fully discussed[5,6]. Aluminium alkoxides were prepared by treating metallic aluminium with the appropriate alcohol, and the alkoxides of tantalum and niobium by treating the chlorides of the metals with alcohols.

Analysis for trace impurities in the starting materials and in the final products showed a decrease in concentration by 1–2 orders of magnitude. This purification is due both to the selectivity of the method of synthesis and to the efficiency of the separation during distillation of the alkoxides, resulting from the large difference in volatility between the main product and the impurities. The total concentration of trace impurities (Ag, Ti, Fe, Pb, Mn) in the Ta and Nb alkoxides was 1×10^{-4} wt.%.

Existing data on the behaviour of trace impurities during the synthesis of various types of MOC indicate not only that transition metals are separated from non-transition metals (and *vice-versa*), but also that the concentration of all trace elements in the final product is very substantially decreased. We can therefore conclude that the methods used to prepare MOC have a high selectivity.

The reactions used in the preparation of metal carbonyls, widely applied in the production of super-pure metals, have a specially high selectivity. With an iron ore containing a large amount of impurities as the raw material, the synthesis of iron carbonyl almost completely eliminates[7] impurities such as S, P, Mn, As, and Cu. The resulting iron carbonyl contains other metal carbonyls as the only impurity. For example, the concentration of nickel in iron pentacarbonyl is $\sim 1 \times 10^{-2}$%. The vapour pressure of nickel tetracarbonyl is appreciably higher than that of iron pentacarbonyl, which allows the nickel content to be decreased to 1×10^{-4}–2×10^{-4}% by bubbling an inert gas through the iron pentacarbonyl at 40–60° and finally redistilling the product[7].

Umilin and Tsinovoi[8] have described some interesting observations on the removal of organic impurities during the synthesis of MOC. Tetrabutyltin was prepared from stannic chloride and a butyl magnesium halide. The butyl bromide was analysed chromatographically, and found to contain various homologues and isomers (1 mole.% of combined s- and t-butyl bromides, 7×10^{-2}% of n- and isopropyl bromides, 4.0×10^{-2}% of ethyl bromide). These impurities react with magnesium to form the appropriate alkyl magnesium bromides, which then react with stannic chloride to give compounds of the general formula $R'_nSnR''_{4-n}$, where R′ and R″ are s-Bu, t-Bu, n-Pr, i-Pr, and Et. Chromatographic analysis of the resulting tetrabutyltin showed that the total amount of organotin compounds containing the isobutyl radical, the propyl radical, and the ethyl radical had been reduced to $\sim 1 \times 10^{-1}$, $\sim 5.3 \times 10^{-5}$, and 3.3×10^{-4}% respectively. These results indicate a purification from organic impurities by 1–2 orders of magnitude during the synthesis of tetrabutyltin.

The purity of the MOC used to prepare super-pure materials must be of the highest order. When the MOC is thermally decomposed any trace impurities of other elements are transferred almost quantitatively to the final metal or compound, whether produced as a powder or as a coating. Therefore the purity of the ultimate product is largely determined by the concentration of trace elements in the original MOC. Purity of the initial MOC is vitally important in the preparation of semiconductor compounds ($A^{II}B^{IV}$, $A^{III}B^{V}$, etc.). The need for extreme purity is particularly evident in the preparation of semiconductor compounds (gallium arsenide) in the form of epitaxially grown layers[9,10]. In addition to traces of other elements, the MOC may contain organic impurities such as the initial reagents or solvents used in their synthesis. These impurities are less harmful than traces of other elements to the electro-physical properties of the resulting materials. However, the contamination of super-pure materials produced by the decomposition of MOC with carbon, resulting from deep-seated chemical changes in the organic compounds, is determined mainly by the type and the structure of the MOC and by the conditions under which these compounds are thermally decomposed. These problems are discussed in detail in Section III.

Another aspect of the MOC purity problem is the "individuality" of the compound, i.e. the presence or absence of homologues of the organic compound or of any other derivative of the metal. The presence of impurities in the form of homologues is determined by the type of MOC and by the method of synthesis used. Thus, metal alkyls produced by the Grignard reaction are, effectively, individual compounds, free from other organic derivatives of the same metal, if the starting reagents are sufficiently pure. The same is not true of alkyl-substituted bis-arene compounds of the transition metals[11–14]: for example, alkyl-substituted bis-benzenechromium is always obtained as a mixture of homologues, due to transalkylation of the alkyl-substituted aromatic hydrocarbons in the presence of the aluminium chloride added to the reaction mixture. Thus, the synthesis of bis-ethylbenzenechromium yields[13,14] a mixture of mono-, di-, and trisubstituted homologues of bis-benzenechromium, as well as a series of asymmetric products such as benzene-ethylbenzenechromium. The concentration of homologues in the mixture is determined by the experimental conditions, varying from fractions of one percent to tens of percent. The preparation of chromium coatings from these complex mixtures is not an easy process: the MOC vapour from the evaporator is led into the reactor, where it flows over the objects to be coated, which are held at a temperature higher than the decomposition temperature of the organochromium compound. The MOC decomposes on the hot surface, and a chromium film is formed. However, since the various organochromium compounds present in the mixture have different boiling points and vapour pressures, and also different decomposition temperatures, it is difficult to maintain a constant concentration of chromium MOC vapour in the reactor, and therefore the rate of deposition and the electro-physical parameters (such as resistivity) of the

film are not easily controlled. Hence, it is necessary to separate the bis-arene compounds of transition metals into their individual compounds before attempting to prepare metallic coatings by the thermal decomposition of these materials.

Table 3. Organic impurities in bis-ethylbenzenechromium, and sensitivity of the gas–liquid chromatography method of analysis used.

Impurity	Impurity content, mol.%	Analytical sensitivity, mol.%
Benzene	1.0	$1.2 \cdot 10^{-2}$
Toluene	$1.0 \cdot 10^{-2}$	$1.0 \cdot 10^{-2}$
Ethylbenzene	1.8	$6.0 \cdot 10^{-3}$
o-Ethyltoluene	$1.0 \cdot 10^{-2}$	$1.0 \cdot 10^{-2}$
o-Diethylbenzene	1.0	$5.1 \cdot 10^{-3}$
Triethylbenzene	$5.0 \cdot 10^{-1}$	$7.2 \cdot 10^{-3}$
bis-Benzenechromium	$5.0 \cdot 10^{-2}$	$6.0 \cdot 10^{-2}$
bis-Toluenechromium	$4.0 \cdot 10^{-2}$	$4.0 \cdot 10^{-2}$
Benzene-ethylbenzenechromium	12.2	$1.9 \cdot 10^{-2}$
bis-Ethylbenzenechromium	66.5	—
Ethylbenzene-*o*-diethylbenzenechromium	15.7	$3.0 \cdot 10^{-2}$
bis-Diethylbenzenechromium	1.5	$5.1 \cdot 10^{-2}$
bis-Triethylbenzenechromium	$6.0 \cdot 10^{-2}$	$6.0 \cdot 10^{-2}$

The most detailed studies of the preparation of bis-arene compounds of the transition metals in a high state of purity have been made on bis-ethylbenzenechromium [13,14]. The results of a gas-chromatographic analysis of one sample of this material are summarised in Table 3.

Benzene-ethylbenzenechromium, bis-ethylbenzenechromium, and ethylbenzene-*o*-diethylbenzenechromium with an impurity content of 6×10^{-2}% have been isolated by fractional distillation of bisethylbenzenechromium.

Bis-arene compounds of chromium can be purified by recrystallisation as well as by fractional distillation. The methyl homologues of bis-benzenechromium in an oxidised form (e.g. as iodides) are crystalline compounds having different solubilities in water, and hence it is possible to prepare alkyl-substituted derivatives of bis-benzenechromium in a relatively high state of purity [5].

Intensive purification of MOC from traces of other elements can be achieved by distillation, fractionation, preparative chromatography, recrystallisation, ion exchange, or extraction. A particularly successful method [15] of extraction of small amounts of one element in the presence of large amounts of another element, whether in order to concentrate the impurity or to purify the major constituent, depends on the formation of inner complexes of the elements. An exchange reaction occurs during the extraction, and as a result the element E′ present in the aqueous phase displaces the element E″ present in the complex. These exchange reactions offer a high selectivity, since the elements which displace E″ are those which are most readily extracted.

Separation of impurities by extraction can be realised in two ways: either by extracting the impurity or by extracting the major constituent and leaving the impurity in the aqueous layer.

Pure cobalt has been prepared [15,16] by the following procedure: an aqueous solution of a cobalt salt is treated with a solution of a cobalt soap (fatty acid salt) in an organic solvent. Impurities whose soaps are more stable than that of cobalt displace cobalt by ion exchange and are transferred to the organic layer. Cobalt solutions containing only traces of iron and copper, and $2–5 \times 10^{-3}$ g litre^{-1} of nickel, have been prepared by this method.

Tetraethoxysilane has been purified from traces of copper, nickel, cobalt, iron, manganese, and other impurities by a complex-adsorption method [17], in which the starting material is treated with sodium diethyldithiocarbamate, which complexes a large number of metals, and the resulting chelates are removed (together with the excess of reagent) by sorption on activated charcoal. Hydrolysis of the tetraethoxysilane purified in this way, followed by heating the resulting silica gel at 650–750°, has yielded samples of silicon dioxide containing aluminium, iron, copper, lead, and other impurities at the $10^{-5}–10^{-6}$ wt.% level.

Clearly, only some of the impurities can be removed from the main element by exchange–extraction methods. Elements whose extraction properties are inferior to those of the main element cannot displace the latter from its compound in the organic phase, and they remain in the aqueous layer.

A more effective method, capable in principle of removing almost any impurity from the aqueous solution has been described by Zolotov and Spivakov [15]. It consists of two main steps. In the first step the main element is extracted in such a way that the whole of the reagent is used up (the excess of the main element need not be very large). All the elements which are extracted less strongly than the main element remain in the aqueous layer. The main element is then re-extracted with an aqueous solution of appropriate acidity, and the pH of the aqueous extract is adjusted to the value used for the initial extraction. The remaining impurities are then extracted (step 2) with the same reagent but in much smaller amount, so that the main element is present in large excess over the reagent. This operation removes the trace elements which can displace the main element from the complex. Practically all metal impurities in zinc chloride and indium nitrate have been removed by this method.

Some examples of the preparation of super-pure metal-organic compounds by different methods are listed in Table 4.

III. METHODS OF DECOMPOSITION OF METAL-ORGANIC COMPOUNDS AND PURITY OF THE PRODUCT

The preparation of pure substances from MOC is based on the ability of these compounds to yield pure metals or compounds under the influence of various forms of energy. The most widely used and better understood methods rely on the decomposition of MOC in the vapour phase by heat, by an electron beam, by the radiation from optical quantum generators, by a gas-discharge plasma, and also by hydrolytic methods in solution.

Depending on the chosen method of decomposition, and on the experimental conditions, the pure substances can be obtained as powders, films (amorphous or polycrystalline), or as single crystals.

The following types of MOC have been used to prepare high-purity materials: metal alkyls and aryls; alkoxides, acetylacetonates, and organic salts; carbonyls, arenes, and some other compounds.

Whereas the purity of the ultimate product in terms of traces of other elements is determined by the purity of the MOC, the problem of contamination by carbon is more complicated and depends on a number of factors.

The general use of MOC for the preparation of pure metals, oxides, and particularly semiconductors was originally thought to be unlikely because of the presence of organic side-products and of the consequent danger of contamination of the final product by carbon and hydrogen.

Table 4. Purity of metal-organic compounds purified by different methods.

MOC	Method of purification	Impurity content, wt.%	Reference
1	2	3	4
$(C_6H_6)_2Cr$	As prepared	Al $2{,}6\cdot10^{-4}$, Cd $2{,}2\cdot10^{-4}$ Cu $3{,}1\cdot10^{-3}$, Fe $2{,}7\cdot10^{-2}$, Mg $1{,}1\cdot10^{-3}$, Mo $1{,}4\cdot10^{-3}$, Si $4{,}1\cdot10^{-3}$	18
$(C_6H_6)_2Cr$	Recrystallised	Al $2{,}6\cdot10^{-4}$, Cd$<2{,}2\cdot10^{-4}$, Cu $1{,}0\cdot10^{-3}$, Fe $2{,}7\cdot10^{-3}$, Mg $4{,}6\cdot10^{-4}$, Mo $1{,}4\cdot10^{-3}$	18
$(C_6H_6)_2Cr$	Recrystallised and sublimed	Cd $2{,}2\cdot10^{-4}$, Cu $1\cdot10^{-3}$, Fe $9\cdot10^{-4}$	18
$(C_6H_6)_2Cr$	Reduction of bis-benzene-chromium iodide	Cu$<5\cdot10^{-5}$, Ti$<1\cdot10^{-3}$, Ni$<1\cdot10^{-3}$, Co$<2\cdot10^{-3}$, Mg $1\cdot10^{-4}$, Mn$<1\cdot10^{-4}$, Al $2\cdot10^{-4}$	5
$(EtC_6H_5)_2Cr$	Distillation	Organic impurities $\leq 6\times10^{-2}$	13, 14
$C_6H_6CrC_6H_5Et$	ditto	ditto	13, 14
$EtC_6H_5CrC_6H_4(C_6H_5)_2$	,,	,,	13, 14
$(EtC_6H_5)_2Cr$	Distillation	Al$<1\cdot10^{-4}$, Mg $3\cdot10^{-4}$, Mn $3\cdot10^{-4}$, Si$<1\cdot10^{-3}$, Ni$<1\cdot10^{-3}$, Fe$<1\cdot10^{-3}$, Ti$<1\cdot10^{-3}$	2
$(C_6H_6)_2CrI$	Crystallisation	Cu$<5\cdot10^{-5}$, Ti$<1\cdot10^{-3}$, Ni$<1\cdot10^{-4}$, Co$<2\cdot10^{-3}$, Mg $7\cdot10^{-4}$, Mn$<1\cdot10^{-4}$, Al $8\cdot10^{-4}$	5
$(C_6H_6)_2CrBr$	ditto	Cu $2\cdot10^{-4}$, Ti$<1\cdot10^{-3}$, Ni $6\cdot10^{-4}$, Co$<2\cdot10^{-3}$, Mg $4\cdot10^{-3}$, Mn$<1\cdot10^{-4}$, Al $6\cdot10^{-3}$, Fe$<2\cdot10^{-4}$	5
$(CH_3C_6H_5)_2CrI$	,,	Cn $4\cdot10^{-5}$, Ti$<1\cdot10^{-4}$, Ni $5\cdot10^{-4}$, Mg $4\cdot10^{-4}$, Mn $9\cdot10^{-5}$, Al $4\cdot10^{-4}$, Fe $1\cdot10^{-3}$	5
$[(CH_3)_3C_6H_3]_2CrI$	,,	Cu $2\cdot10^{-3}$, Ti$<2\cdot10^{-3}$, Ni $2\cdot10^{-3}$, Mg $1\cdot10^{-3}$, Mn$<5\cdot10^{-4}$, Al $6\cdot10^{-4}$, Fe $7\cdot10^{-4}$	5
$(CH_3)_3Ga$		Cu $6\cdot10^{-5}$, Mg $5\cdot10^{-5}$, Zn $2\cdot10^{-4}$, Al $1\cdot10^{-4}$, Ti $1\cdot10^{-4}$, Si $2\cdot10^{-4}$, Sb $9\cdot10^{-5}$, Pb $3\cdot10^{-4}$, Cr$<4\cdot10^{-6}$, Mn $2\cdot10^{-6}$, Fe $9\cdot10^{-5}$, Ni $5\cdot10^{-5}$, Ag$<3\cdot10^{-6}$	2
$(CH_3)_3GaO(C_2H_5)_2$	ditto	Cu $5\cdot10^{-5}$, Mg $6\cdot10^{-5}$, Zn $4\cdot10^{-4}$, Al $2\cdot10^{-4}$, Ti$<1\cdot10^{-4}$, Si $2\cdot10^{-4}$, Sn $4\cdot10^{-4}$, Pb $4\cdot10^{-3}$, Cr$<4\cdot10^{-6}$, Mn$<2\cdot10^{-6}$, Fe $4\cdot10^{-4}$, Ni $1\cdot10^{-4}$, Ag$<3\cdot10^{-6}$	2,19
$(C_4H_9)_4Sn$	Distillation	Organic impurities $<5\times10^{-4}$	8
$Si(OC_2H_5)_4$	Extraction and absorption	Al $3\text{—}8\cdot10^{-6}$, Fe $2\cdot10^{-6}$, Mg $2\text{—}8\cdot10^{-6}$, Mn $1\cdot10^{-6}\text{—}3\cdot10^{-7}$, Cu $2\cdot10^{-6}\text{—}8\cdot10^{-7}$, Pb $5\cdot10^{-6}$, B$\sim2\cdot10^{-6}$	17
$Al(O\text{-}i\text{-}C_3H_7)_3$	Distillation	Cu $7\cdot10^{-5}$, Mg $4\cdot10^{-4}$, Ag $4\cdot10^{-4}$, Ti$<3\cdot10^{-4}$, Fe $5\cdot10^{-4}$, Pb$<1\cdot10^{-4}$, Mn$<2\cdot10^{-5}$	5,6
$Ta(OC_2H_5)_5$	ditto		5,6
$Nb(OC_2H_5)_5$	,,	Ag$<1\cdot10^{-5}$, Fe $3\cdot10^{-4}$, Pb$<2\cdot10^{-3}$, Mn$<2\cdot10^{-4}$	5,6

This may be the reason why no attempt was made for many years to prepare semiconductor materials from MOC: only very recently has the successful use of metal-organic compounds in the preparation of semiconductor materials such as epitaxially grown $A^{II}B^{VI}$ and $A^{III}B^{V}$ structures been reported.

A number of approaches which may help to minimise or even to eliminate the risk of carbon contamination may be found in the large fund of experimental information on the decomposition of metal-organic compounds. This belief is confirmed by the many recent reports of the preparation of ultra-high purity materials from MOC. There are two ways of controlling the residual carbon content of materials prepared from MOC. The first relies on the correct choice of MOC and on appropriate control of the decomposition conditions. The second relies on special treatment of the final products obtained from the MOC.

The criteria which determine the best type of MOC structure are the mechanism of thermal decomposition and the likelihood of carbon contamination of the final product.

The decomposition reactions of MOC can be described by the following mechanisms:

1) radical $R_nE \rightarrow n\dot{R} + E$,
2) hydride or olefin $(RCH_2CH_2)_nE \rightarrow nRCH{=}CH_2 + E + H_2$,
3) molecular $L_nE \rightarrow nL + E$.

The first two types of decomposition are typical of alkyl, aryl, and cyclopentadienyl compounds, the third is typical of MOC formed by molecules containing an even number of π-electrons. The most important among the latter are arene and carbonyl compounds of the transition metals, in which the ligands are aromatic hydrocarbons or carbon monoxide.

Side reactions involving the organic radicals and molecules formed during the decomposition of the MOC may lead to contamination of the resulting metal with carbon. Among the most important secondary reactions of the radicals formed by thermal dissociation of MOC, which may influence the purity of the metal produced, are the decomposition of an organic radical to an olefin and hydrogen, or decomposition with C–C bond breaking. Both these reactions have been detected in a study[20,21] of the thermolysis of MOC of tin, germanium, and aluminium. The conclusion of this study was that the lower alkyl radicals tend to decompose by splitting a C–C bond, the higher radicals by splitting a C–H bond.

The influence of the alkyl radical on the purity of the product of MOC decomposition is clearly shown by the behaviour of aluminium-organic compounds[21]. Thus, whereas the pyrolysis of trimethylaluminium is a method of preparation of aluminium carbide, high-purity aluminium containing $\sim 1\times10^{-2}\%$ of carbon can be prepared by thermal decomposition of tri-isobutylaluminium. A similar behaviour is observed also in the thermal decomposition of organogallium compounds: whereas the decomposition of trimethylgallium is accompanied[22] by the formation of a polymeric product of composition $(CH_3Ga)_n$, high-purity gallium metal is obtained from the decomposition of tri-isobutylgallium[5].

Thus, to prepare pure metals by thermal decomposition of MOC we must choose compounds in which the E–R bond energy is small, and the side-reactions of the organic constituents of the molecule occur preferentially by β–C–H (rather than β–C–C) cleavage.

MOC which decompose by the molecular mechanism are suitable for the preparation of pure metals in the form of powders or in the form of coatings. These include bis-arene, arenecarbonyl, carbonyl, and some other organic compounds of the transition metals. The influence of the starting MOC on the carbon and hydrogen content of chromium and molybdenum films prepared pyrolytically has been carefully studied[23–25]. The study included a

series of bis-arene compounds of chromium and molybdenum, the iodides of the bis-arene derivatives of chromium, and some arenetricarbonyl compounds of both metals. The resulting metal films were found to be contaminated by carbon, hydrogen, and (in the case of chromium) oxygen. The chromium films contained between 0.5 and 10% of carbon. The carbon content increased from the arene π-complexes to the arenetricarbonyl compounds of chromium, and within the chromium arene series it increased with the number of alkyl substituents in the aromatic nucleus of the π-complex. The lowest carbon content was found in the chromium films prepared by the pyrolysis of the iodides of bisarenechromium compounds.

Molybdenum films prepared by thermal decomposition of bis-arene and arenetricarbonyl compounds of molybdenum contain more carbon than chromium films prepared under similar conditions from analogous compounds.

Oxygen analysis of the chromium and molybdenum films gave some interesting results. Thus, whereas the pyrolytic chromium films contained 8% of oxygen as Cr_2O_3, the molybdenum films prepared by pyrolysis of bisarenemolybdenum complexes under similar conditions contained no oxygen. The most likely explanation is that both chromium and molybdenum are readily oxidised in the presence of a trace of oxygen, but whereas the chromium oxide is involatile and resistant to reduction by the products of partial decomposition of the MOC, the molybdenum oxide is more volatile, and can be reduced to the metal at temperatures as low as 360–700°.

Evidently, the presence of carbides and oxides in the pyrolytic chromium films can explain their enhanced hardness, mechanical strength, and resistance to acids (as compared with chromium films prepared electrochemically or by vacuum deposition).

It is clear from these results that the purity of metals prepared by thermal decomposition of MOC is largely determined, as far as carbon contamination is concerned, by the type of compound used, and that this contamination can be partly or completely eliminated by suitable choice of the starting compound.

However, the experimental conditions under which the MOC is thermally decomposed are also a very important factor in determining the purity (and in particular the freedom from carbon) of the resulting metals and compounds. Among the most important practical conditions are factors such as the medium, the decomposition temperature, the total pressure in the reactor, the rate of removal of the decomposition products, and the possibility of catalytic reactions.

The temperature at which thermal decomposition is carried out has a profound effect on the decomposition mechanism of the MOC, on the direction and extent of side-reactions, and hence on the purity of the final product.

Work on the bis-arene compounds of chromium and molybdenum has shown that the carbon content of the metal film increases with the temperature at which the MOC is decomposed. Thus, if bis-ethylbenzenechromium is pyrolysed at temperatures in the range 450–700° the carbon content of the chromium films increases from 0.7 to 6%,[23] and in the decomposition of mesitylenetricarbonylmolybdenum it increases from 6 to 10% as the temperature is increased from 400 to 550°.[25]

The higher carbon content is the result of more deep-seated chemical changes in the aromatic hydrocarbons, leading to the formation of free carbon and metal carbides. It is important to note that the aromatic ligands in arene compounds of the transition metals suffer more drastic decomposition than the corresponding aromatic hydrocarbons. Thus, hydrogen evolution is hundreds of times more abundant during the decomposition of bis-benzenechromium than during the decomposition of benzene at the same temperature[18].

A thermodynamic analysis of the decomposition of bis-benzenechromium[26] has shown that reactions leading to the formation of chromium, chromium carbides, and free carbon have a higher probability than reactions in which the only solid products are chromium and carbon. The higher the temperature, the greater is their probability. Hence, the decomposition temperature chosen for the bis-benzenechromium should be as low as possible in order to minimise the carbon content of the chromium films.

An increase in the temperature at which metal-organic compounds are thermally decomposed does not invariably produce an increase in the carbon content of the film: the type of MOC, and the nature of the decomposition products, determine the effect of an increase in temperature. This phenomenon is clearly illustrated by the preparation of pure metals through the pyrolysis of metal carbonyls[27–29]. The decomposition of molybdenum hexacarbonyl by the reaction $Mo(CO)_6 \rightarrow Mo + 6CO$ is accompanied by the side-reaction $2CO \rightleftharpoons C + CO_2$, which is responsible for the contamination of the molybdenum with carbon. On raising the temperature, the equilibrium of the carbon monoxide decomposition reaction is shifted towards the left, and the amount of free carbon decreases. Several workers[27–29] have found that molybdenum coatings prepared by thermal decomposition of molybdenum hexacarbonyl at relatively high temperatures have a lower carbon content.

It follows that a knowledge of the decomposition mechanism of the MOC, and of the side-reactions, is an essential prerequisite to the correct choice of decomposition temperature for the preparation of pure, carbon-free metals. The decomposition temperature can be lowered very significantly by introducing various additives into the reactor: this is an interesting method of decreasing the probability of contamination of a metal or compound prepared by thermal decomposition of MOC. The effect of additives can be explained as follows. An additive can react with the starting reagent, or it can catalyse its decomposition, thus lowering the decomposition temperature of the MOC. It can also react with the decomposition products of the MOC, thus lowering the probability of the side-reactions and raising the purity of the product. Lastly, the additive may deactivate the excited metal atoms formed by the thermal decomposition of the MOC, and modify the crystallisation conditions. Thus, the addition of amines during the thermal decomposition of tetra-alkylgermanium compounds has been shown[30] to favour the growth of monocrystalline germanium "whiskers".

The decomposition temperature of bis-arenechromium compounds can be lowered by using halogen and sulphur compounds as catalytic additives[31,32].

In the thermal decomposition of tetraethoxysilane, the presence of oxygen lowers the temperature of formation of silicon dioxide by ~300°. The catalytic effect of transition-metal salts can give rise to autocatalysis in the decomposition of some MOC. Thus, a chromium halide is formed by disproportionation during the preparation of chromium coatings from halogen derivatives of bis-arenechromium compounds[23,33]; this halide catalyses the thermal decomposition, lowering the formation

temperature of the chromium film and at the same time decreasing its carbon content.

The pressure, and the rate of removal of by-products, have a major influence on the quality and the structure of deposits prepared by thermal decomposition[34]. The pyrolysis of MOC gives rise to gaseous products whose vapour pressure is much higher than the vapour pressure of the original MOC. As a result, the total pressure in the system increases, and the concentration of MOC close to the substrate surface decreases: both these effects tend to lower the rate of deposition. This rate-limitation by pressure is observed at constant rate of removal of the reaction products. If the rate of removal is zero (closed reaction vessel) there is a gradual decrease in deposition rate due to the increase in pressure in the system. If the rate of removal of the decomposition products tends to infinity the rate of growth of the deposit becomes independent of pressure, and is limited by the rate of mass transfer to the substrate or by the rate of the decomposition reaction of the MOC. In all intermediate cases the rate of deposition is pressure-dependent to a greater or lesser extent. The presence of decomposition products near the substrate surface, and the increase in total pressure, tend to favour the adsorption of the decomposition products on the solid deposit and to hinder their desorption, thus increasing the danger of contamination. These observations lead to the following practical conclusion: in the thermal decomposition of MOC, faster depositions and purer deposits are obtained by working at low pressures and by ensuring that the decomposition products are removed rapidly.

Domrachev and coworkers[34] studied the carbon content of molybdenum films as a function of the ratio of the rate of supply of molybdenum carbonyl to the rate of removal of the reaction products, and they found that the carbon content changes from 4.6 to 1×10^{-1} wt.% as the rate of removal is increased from 0.5 to 14.2 litre s^{-1} (surface temperature 602°, $P = 0.1$ mmHg).

Other factors are also known to affect the purity of metals and compounds prepared by thermal decomposition of MOC. For example, the effect of an electric field on the growth of deposits during the thermal decomposition of molybdenum carbonyl has been investigated[38]. It has been shown that the electrostatic field increases the rate of deposition of the metal, drastically lowers the carbon content (to $\sim 1 \times 10^{-2}$%), and lowers the optimum deposition temperature of high-quality films.

In addition to the thermal decomposition method, the hydrolytic method is widely used for the preparation of high-purity materials from MOC in the vapour phase. The method lends itself to the preparation of very pure oxides, mixed oxides, and compounds such as barium titanate. Hydrolysis can be induced by treating the MOC with water vapour, in solutions, or in the vapour phase. Hydrolysis in solutions occurs at room temperature, and the resulting oxides are practically free from carbon. The greatest danger of carbon contamination arises during hydrolysis in the vapour phase. The purity of silicon dioxide prepared by vapour-phase hydrolysis of tetraethoxysilane is profoundly affected by the ratio $Si(OC_2H_5)_4 : \alpha H_2O$, the optimum value of α being a function of the hydrolysis temperature[37]. Thus, the optimum values of α at 427, 727, and 1227° are 2.85, 4.85, and 6 respectively. As the temperature increases, and as α decreases, the amount of carbon incorporated in the solid deposit increases. Whereas powdered silica prepared at 350° and with $\alpha < 3$ is strongly contaminated with carbon (and black in colour), a fine white powder is obtained at the same temperature with $\alpha > 4$. No carbon is detected in the latter sample by i.r. or u.v. spectroscopy.

Thus, the carbon content of materials prepared by the decomposition of MOC can be lowered by a number of methods, including the choice of the best type of starting material and proper control of the experimental conditions. In addition, the carbon content can also be decreased by special treatment of the final product of thermal decomposition. Hydrogen (and, in particular, moist hydrogen) is a very effective medium for the post-treatment of metals such as chromium, molybdenum, tungsten, iron, nickel, and ruthenium. Thus, whereas molybdenum prepared by the pyrolysis of molybdenum carbonyl contains ~1% of carbon, a hydrogen treatment after pyrolysis lowers the carbon content to 1×10^{-2}.[38] Thermal decomposition of iron carbonyl followed by heat treatment of the resulting carbonyl iron in hydrogen yields the purest of all iron powders[7]. The heat treatment of the carbonyl iron removes nitrogen and oxygen impurities as well as carbon. The main impurities in iron powder prepared by thermal decomposition of iron carbonyl are cementite (Fe_3C), the nitride Fe_4N, and magnetite (Fe_3O_4).[7] These impurities react with hydrogen to give metallic iron and gaseous products (water, methane and ammonia). The impurity hardest to remove is elemental carbon, which begins to react with hydrogen at an appreciable rate only above 400°. The purest iron powder is obtained by treating the carbonyl iron powder in a hydrogen atmosphere at the lowest possible temperatures (in the range 300–400°) in a large excess of hydrogen and with continuous removal of the reaction products[7]. The level of purity attainable in iron powder prepared by thermal decomposition of iron carbonyl followed by heat treatment in a hydrogen atmosphere is indicated in Table 5.

IV. PREPARATION OF PURE ELEMENTS, OXIDES, AND OTHER COMPOUNDS

Elements can be prepared in a high state of purity from MOC by methods such as thermal decomposition in the vapour phase or in solutions, photolysis, and electrolysis. The ultimate freedom from trace impurities is determined by the purity of the initial MOC rather than by the method of decomposition. Contamination of the final product by carbon depends mainly, as discussed in Section III, on the type of MOC and on the decomposition conditions.

The advantages of using MOC for the preparation of pure materials are most clearly seen when the ultrapure material is required in the form of a thin coating, or when an alloy of prescribed composition is deposited as a thin film. Alloy films deposited by conventional methods do not always have the same composition as the starting material, because of differences in the evaporation temperature of the alloy components. By choosing MOC of different metals having similar physicochemical properties, or by adding controlled amounts of MOC vapours to the reactor, coatings having the desired component ratio can be deposited by thermal decomposition even on items of complicated shape.

The relatively low decomposition temperature of MOC, and the absence of other reagents or solvents, ensure that metals prepared from MOC are purer than metal prepared by other methods. Chromium prepared by the

pyrolysis of bis-benzenechromium[18] contains fewer trace impurities than electrolytic chromium. The purity of iron prepared by thermal decomposition of iron pentacarbonyl is outstandingly high[7,39].

Because of the selectivity of the methods of synthesis, and of the high purity of the resulting metals, MOC have been used on an industrial scale to prepare specially pure materials. The carbonyl process for the preparation of pure iron[7] is very widely used in industry. It can be described by the following scheme:

$$Fe_{(impure)} + 5\,CO \xrightarrow[P=100-200\ atm]{180-220^\circ} Fe(CO)_5 \xrightarrow{230-330^\circ} Fe_{(pure)} + 5\,CO\,.$$

In the first step of the process the carbon monoxide reacts selectively with an iron-containing ore to give iron pentacarbonyl: this results in considerable purification from traces of other metals. In the second step, pure iron is produced by thermal decomposition and the carbon monoxide is re-cycled.

Table 5. Summary of preparation of pure substances from metal-organic compounds.

Element or compound	Starting compound	Method and conditions	Trace impurities in the product	Reference
1	2	3	4	5
Al	Di-isobutylaluminium hydride	Pyrolysis at 340°	Carbon $< 2 \times 10^{-2}$	21
	Tri-isobutylaluminium	Pyrolysis at 200°	Purity 99.999	50
	Complex of triethylaluminium with sodium fluoride	Electrolysis with lead anode	High purity	50
In	Trimethylindium complexes	Electrolysis	Cu 5×10^{-5}, Cd 2×10^{-4}, Tl 1.4×10^{-5} wt.% Fe, Pb, Sn, Ag, Mg, Si, Ni not detected	51,52
Ga	Triethylgallium	Electrolysis	Pb $\ll 1 \times 10^{-4}$, Zn 4×10^{-6}, Cu 8×10^{-6}, wt.% Sn, Mn not detected	51,52
Tl	Organic complexes of thallium salts	Electrolysis	Al 9×10^{-5}, In 8×10^{-4}, Mg 3×10^{-5} wt.% Ag, Cu, Fe, Si not detected	51,52
Ge	Germanium tetra-alkyls	Pyrolysis at 400°	Carbon < 0.1%	53,54
Fe–Ni	Mixed iron and nickel carbonyls	Pyrolysis below 200°	Carbon < 0.001%	55
Fe	Carbonyl iron	Pyrolysis and heating in hydrogen	Ni $1-2 \times 10^{-4}$ C $< 3 \times 10^{-3}$ C 1×10^{-2} S, P, Cu, Mn	7
	ditto	Pyrolysis at 200–300°	Ni, Co, Cr, Mo, Zn, Si not detected	39
Ru	Dicyclopentadienylruthenium	Pyrolysis at 595° in hydrogen	Ru 99.99% pure Fe 1×10^{-2}, Pd $< 5 \times 10^{-3}$, Bi, Si even smaller traces	56
W	Tungsten carbonyl	Pyrolysis at 1000°	Carbon 0.02 wt.%	57
Cr	bis-Cumenechromium	Pyrolysis at 300–400°	Carbon < 0.2%	58
	bis-Ethylbenzenechromium	Pyrolysis	Al 6×10^{-3}, Fe 3×10^{-3}	59
	bis-Benzenechromium	Pyrolysis	Cu $6,1 \times 10^{-4}$, Mo 1.85×10^{-4}, Sn 6.9×10^{-4}, C 1.06×10^{-1}, O 2.04×10^{-2}, H 5.7×10^{-4} N 2.16×10^{-3}; Al, Cd, Fe, Mg, Si not detected	18
Mo	Molybdenum carbonyl	Pyrolysis and heating in hydrogen	Carbon 1×10^{-2}%	38
Mo	ditto	Pyrolysis in an electric field at 600–1200°	Carbon $< 1 \times 10^{-3}$%	36
Ni	Nickel carbonyl	Pyrolysis in the presence of hydrogen sulphide below 100°	C 0.01%	60,61
Ni	Nickel carbonyl	Pyrolysis and heating in wet hydrogen	Mg, Si, P, S 1×10^{-3} Co, Zn, 5×10^{-4}, Cd, Sn, Sb, Pb, Bi, Al 3×10^{-4}, Fe 2×10^{-2} C trace	62

Table 5 (cont'd)

Element or compound	Starting compound	Method and conditions	Trace impurities in the product	Reference
1	2	3	4	5
Ga	Tri-isobutylgallium	Pyrolysis at 200°	Zn $< 1 \times 10^{-3}$, Ag 2×10^{-4}, Cu 4×10^{-5}, Al 1×10^{-4}, Ni $< 1 \times 10^{-3}$, Fe $< 1 \times 10^{-3}$, Cr $< 1 \times 10^{-3}$, Mg 4×10^{-5}, Mn $< 1 \times 10^{-4}$	5
SiO_2	Tetraethoxysilane	Hydrolysis and heating at 650–750°	Al $3-8 \times 10^{-6}$, Fe 2×10^{-6} Mg $2-8 \times 10^{-6}$ Mn $1 \times 10^{-6}-3 \times 10^{-6}$ Cu $2 \times 10^{-6}-8 \times 10^{-7}$, Pb $\sim 5 \times 10^{-6}$, B 2×10^{-6}	17
HfO_2	Hafnium tetra-amyloxide	Hydrolysis, 24 h drying at 50°, 0.5 h heating at 250°	99.995%	63
Al_2O_3	Aluminium tri-isopropoxide	Hydrolysis	Cu 7×10^{-5}, Mg 4×10^{-4}	5,6
Ta_2O_5	Tantalum penta-ethoxide	Hydrolysis	Ag $< 4 \times 10^{-4}$, Ti $< 3 \times 10^{-4}$, Fe 5×10^{-4}, Pb $< 1 \times 10^{-4}$, Mn $< 2 \times 10^{-5}$	5,6
Nb_2O_5	Niobium penta-ethoxide	Hydrolysis	Ag $< 1 \times 10^{-5}$, Fe 3×10^{-4}, Pb $< 2 \times 10^{-3}$, Mn $< 2 \times 10^{-4}$	5,6
$BaTiO_3$	Barium isopropoxide, titanium tetra-t-amyloxide	Hydrolysis	99.98%	44
$HfTiO_4$	Hafnium tetra-amyloxide, titanium tetra-amyloxide	Hydrolysis, 12 h drying at 50°, heating at 580°	99.95% Co $< 1 \times 10^{-3}$, Na $< 5 \times 10^{-3}$, Si $< 3 \times 10^{-3}$, Fe $< 3 \times 10^{-3}$	64
$HfO_2Y_2O_3$	Hafnium tetra-amyloxide, yttrium tri-isopropoxide	Hydrolysis, 12 h drying 60°, 0.5 h heating at 550°	99.95%	65
GaAs	Trimethylgallium, arsine	Pyrolysis	Si 8.6×10^{-5}, S 3.4×10^{-5}, Fe 6.2×10^{-5}, Cu 1×10^{-5}, Zn 4×10^{-5}, C 2×10^{-3}, Ni 1.7×10^{-5}, O 2.4×10^{-3}	10
CdS	Dimethylcadmium, hydrogen sulphide	Pyrolysis	Semiconductor purity	47–49
	ditto	Reaction in solution		46
AlAs single crystal	Trimethylaluminium	Thermal decomp. at 700° in arsine	Semiconductor purity	67
AlP single crystal	ditto	Thermal decomp. at 700° in phosphine	ditto	67
GaP single crystal	Triethylgallium, triethylphosphine	Thermal decomp. at 420° of a mixture of triethylgallium and triethylphosphine	"	68
ditto	Trimethylgallium	Thermal decomp. at 700° of trimethylgallium in the presence of phosphine	"	9
AlN	Trimethylaluminium	Decomp. at 1200° of trimethylaluminium in ammonia	"	69
GaN	Trimethylgallium	Decomp. at 925–975° in ammonia	"	69
Fe_2O_3	Iron carbonyl	Oxidation	High purity	7
Ge	Tetraethylgermanium	Thermal decomp. at 820° in argon–hydrogen mixture	Semiconductor purity no carbon detected	66

A study of the thermal decomposition of tri-isobutylaluminium

$$[(CH_3)_2CH{-}CH_2]_3Al \rightarrow 3(CH_3)_2C{=}CH_2 + {}^3/_2H_2 + Al$$

has shown[40] that a method of purification of aluminium similar to the carbonyl iron process could be developed by combining the dissolution of technical-grade aluminium in isobutylene in the presence of hydrogen with the decomposition of isobutylaluminium. Some complications arise from the possible contamination of the aluminium with carbon, but the carbon content can be made as low as 2×10^{-2}% by suitable choice of the conditions under which the tri-isobutylaluminium is decomposed[21].

Pure metal oxides and other compounds can be prepared from MOC by methods such as thermal decomposition in the vapour phase of one (or several) compounds, reaction of MOC in solutions or in the vapour phase with oxygen or with compounds having labile hydrogen atoms (hydrogen sulphide, arsine, stibine, phosphine), hydrolysis in the vapour phase or in solution, or decomposition in the plasma of a gas discharge.

Depending on the conditions under which the MOC is decomposed, oxides and semiconducting compounds can be obtained in the form of powders, films, or epitaxially grown layers.

The most convenient sources of pure oxides are metal alkoxides and salts of organic acids.

The hydrolytic decomposition of alkoxides is widely used for the preparation of high-purity metal oxides. This method yields not only powdered oxides and mixed oxides, but also thin films for coating optical surfaces, for protective coatings, and for use as diffusion sources in semiconductor technology[41].

The hydrolytic method has been used to prepare very pure oxides of silicon[17], germanium[42], magnesium, aluminium, and titanium[43]. Very pure mixed oxides and compounds can be obtained by hydrolysing several alkoxides simultaneously. Thus, the hydrolysis of a mixture of barium isopropoxide and titanium tetra-amyloxide yields[44] barium titanate of 99.98% purity and 50–100 Å particle size:

$$Ba(OC_3H_7)_2 + Ti(OC_5H_{11})_4 + 3H_2O \rightarrow BaTiO_3 + 2C_3H_7OH + 4C_5H_{11}OH.$$

The uniformity and stoichiometric composition of the product were confirmed by chemical analysis and electron microscopy. The powder, dried at 50° in an inert gas atmosphere, was shown to have the barium titanate structure by X-ray diffraction analysis and i.r. spectroscopy.

Powders or films consisting of mixed oxides in the required proportions can be prepared from the alkoxides of Group IV elements such as silicon and titanium, and also aluminium. Simultaneous hydrolysis of solutions of tetraethoxysilane and compounds of other elements has been used to prepare powders and glasses of various compositions[45]. Calculated compositions of the oxides in solution were found to agree satisfactorily with the experimentally observed compositions of the powders obtained by hydrolysis[45].

The film-forming component (e.g. the alkoxide) must be suitably chosen to ensure that the oxide is deposited as a film. Tetraethoxysilane and some inorganic compounds are used in solution in polar organic liquids, aqueous alcohol, or acetone–water mixtures. The water content varies between 0.1 and 10–20%, depending on the nature of the film-forming compound[41]. Mixtures of polar and non-polar solvents can also be used to prepare films from mixtures of several compounds.

One of the distinguishing features of the use of MOC for the preparation of semiconducting compounds (in contrast to the use of inorganic compounds) is that the purity problems are less intractable. This is because the preparation of semiconductor materials from MOC usually involves lower temperatures than the preparation of the same materials from inorganic compounds, thus minimising the danger of contamination from the material of the apparatus. Furthermore, the selectivity of the methods of preparation of the MOC (discussed in Section II) ensures that many undesirable impurities are eliminated from the starting material.

Like the oxides, other compound semiconductors can be prepared from MOC by decomposition in solution or in the vapour phase. The conditions under which the decomposition is carried out are determined mainly by the form in which the semiconductor is required (powder, deposited film, or epitaxially grown layer).

Pure metal chalcogenides can be prepared by treating MOC in solution with hydrogen sulphide. Hanschild and Glemser[46] have obtained very pure cadmium sulphide by the reaction between dimethylcadmium and hydrogen sulphide in liquid propane:

$$(CH_3)_2Cd + 2H_2S \rightarrow Cd(SH)_2 + 2CH_4$$
$$Cd(SH)_2 \rightarrow CdS + H_2$$

The cadmium hydrogen sulphide decomposes at −(40–50)°; the last traces of hydrogen sulphide are removed by heating the product in a vacuum. The method yields material free from traces of other metals, and it can be used to prepare other binary compounds.

The preparation of pure semiconductor materials from MOC is particularly attractive when the product is required in a special form (for example, an epitaxially grown layer). Epitaxial layers of $A^{III}B^{VI}$ and $A^{III}B^{V}$ semiconductor compounds and of their solid solutions can be prepared by decomposing a MOC in the vapour phase in the presence of the appropriate hydride at a temperature suitable for the growth of a monocrystalline layer.

Thus, epitaxial structures of gallium arsenide have been prepared[9,10] by the thermal decomposition of gallium alkyls in the presence of arsine. The impurity level of the gallium arsenide with respect to Si, S, Fe, Cu, and Zn was 10^{-4}–10^{-5}. It is interesting to note that the carbon contamination in these layers of gallium arsenide[10] is of the same order ($\sim 2 \times 10^{-3}$%) as in the layers prepared from gallium and arsenic chlorides: hence, this contamination cannot be due to the carbon from the MOC. Epitaxial structures of cadmium and zinc sulphides, selenides, and tellurides, of semiconductor purity, have been obtained by the thermal decomposition in the vapour phase of dimethylcadmium and diethylzinc in the presence of hydrogen sulphide or hydrogen selenide, or of dimethyltellurium[47–49].

We may conclude from these examples of the preparation of high-purity materials that the decomposition of MOC is a very promising method of preparation of pure metals, oxides, and compound semiconductors. It lends itself to the production of these materials not only in a pure form, but also in the special configurations required in electronics technology. Rapid developments of the MOC method can be expected in the near future.

Various examples of the preparation of high-purity materials from MOC are listed in Table 5 together with the appropriate conditions.

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In conclusion, we have established that the thermal decomposition of MOC is a powerful method of preparation of various substances in a high state of purity as coatings, films, and single-crystal layers. The method can be applied also to refractory materials. Rapid developments, leading to widespread practical applications, can be expected.

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