Carbonaceous fragments of osmium ligand deficient clusters that take part in alkane C–H and C–C bonds cleavage in the presence of molecular hydrogen

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Received 10 October 1992; accepted 15 April 1993

The direct participation of carbonaceous ligands of osmium ligand deficient clusters (LDC) in alkane and cycloalkane reactions in the presence of H_2 is proved by ^{14}C-labeling. In contrast to the other metallic catalysts, wherein carbonaceous ligands block active centres, the C-containing ligands of the Os-LDC are active and exhibit at least two functions in alkane and cycloalkane reactions: stabilization of clusters against agglomeration and preservation of active centres.

Keywords: $^{14}C/^{12}C$ exchange; alkane C–H and C–C bond activation; carbonaceous ligands; osmium ligand deficient clusters

1. Introduction

Recently we have shown [1,2] that small osmium ligand deficient clusters (Os-LDC) can be prepared in the absence of any polar solvent or stabilizing polymer.

These Os-LDC of 7–16 Å in diameter [3] effectively catalyze hydrogenolysis of alkanes and cycloalkanes at 100–150°C and initial H_2 pressure of 5 MPa, hydrogenation of cyclopentadiene, benzene and toluene at 20°C, multiple H/D exchange between CH_4 and D_2 at 100–120°C and methanation of CO_2 at 150–180°C [2].

In the present work we focus our attention on the role of carbonaceous ligands of these osmium clusters in reactions involving C–H and C–C alkane bond cleavage.

The nature and the role of the carbonaceous species formed over metal atoms in the course of hydrocarbon reactions as well as in many other important processes are the central problems for catalysis.

Mechanistic investigations of heterogeneous catalytic reactions of hydrocarbons on metals in the presence of hydrogen or deuterium, started well before classic

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† Deceased on the 7th of January 1991.

organometallic chemistry, led to evidence for the existence of a large number of different surface organometallic complexes, called by Burwell an "organometallic zoo" [4,5]. However, investigations of the last three decades show that the various reactions (hydrocracking of alkanes and cycloalkanes, H/D exchange between methane and D_2, Fischer–Tropsch and methanol synthesis, methanation of CO and CO_2, hydrogenation of olefins, steam reforming and decomposition of HCOOH) lead to final formation of carbonaceous C_1 fragments bound to metal atoms by single, double or triple bonds.

The characteristics of the Os-LDC are similar to those of Ni- and Co-LDC, prepared by vapour phase synthesis. Hydrogenation of dried Os-LDC at 100–150°C and $P_{H_2} = 0.1$–0.5 MPa yields methane. The reaction of dried Os-LDC with D_2 affords deuteromethanes in the ratio $CD_4 : CD_3H : CH_2D_2 : CH_3D = 1.1 : 1.0 : 1.5 : 0.7$ [2]. Thus, the C_1H_x fragments seem to be also dominant in the Os-LDC, although we cannot completely rule out the possibility of presence of other carbonaceous groups.

In the present paper using the ^{14}C labeling method we tried to get a direct answer to the question, whether the carbonaceous ligands take part in alkane reactions. We studied the $^{14}C/^{12}C$ exchange between $OsCH_x$ and cyclo-$^{14}C_6H_{12}$ and its cracking products, $Os^{14}CH_x$ and pentane and its cracking products, $Os^{14}CH_x$ and methane in the presence or absence of H_2.

2. Experimental

Two series of radiometric runs were carried out. In the first one the specific radioactivities A (in imp.min^{-1} mg^{-1} ($BaCO_3$)) were measured for initial and final products (RH and $OsCH_x$) after combustion of $OsCH_x$ or the mixture of hydrocarbons into CO_2 with following conversion into $BaCO_3$ [6]. In this series the total ^{14}C content in a hydrocarbon mixture was determined. In the second series the ^{14}C content for each volatile compound (α) was measured as a ratio of RGLC[#1]/GLC peaks with a home-made radio-chromatograph. Procedures for Os-LDC preparation have been reported in detail previously [2].

Os-LDC preparation. All operations were carried out under argon atmosphere. The suspension of OsO_4 (0.127 g, 0.5 mmol) in 3.6 g (50 mmol) of pentane was heated at 150°C and initial H_2 pressure of 5 MPa for 15 h in a steel autoclave. Gaseous products were trapped at −196°C and then analyzed by GLC. The catalyst was carefully dried in vacuo and stored under argon.

$Os^{14}CH_x$ preparation. The suspension of OsO_4 (0.25 g, 1 mmol) in 3.9 g (50 mmol) of $^{14}C_6H_6$ with $A = 5864$ was loaded under argon into a steel autoclave. Reduction was carried out at room temperature and initial H_2 pressure of 5 MPa for 3 days with a periodical filling with H_2. When the adsorption of H_2 stopped, all

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[#1] Radio-gas chromatography.

volatile products were separated from the catalyst by evacuation. The catalyst was washed with pentane and carefully dried in vacuo. To determine the radioactivity the samples were burnt to CO_2 with following conversion into $BaCO_3$ and the A values of $BaCO_3$ samples were measured. The resulting cyclo-$^{14}C_6H_{12}$ and $Os^{14}CH_x$ had $A = 5263$ and 465 respectively.

$^{14}C/^{12}C$ exchange between CH_4 and $Os^{14}CH_x$. The evacuated autoclave, containing $Os^{14}CH_x$ with $A = 650$ (0.25 g, 1.08 mmol) was filled with CH_4 (0.12 MPa, 3 mmol) and H_2 (5 MPa). The autoclave was heated at 150°C for 15 h. The resulting methane had $A = 82$. In the similar experiment but in the absence of H_2 methane practically did not contain ^{14}C ($A = 7.2$) after the run.

$^{14}C/^{12}C$ exchange between $Os^{14}CH_x$ and alkane (or cycloalkane). Pentane (1.44 g, 20 mmol) was cracked in the presence of $Os^{14}CH_x$ ($A = 465$) at 150°C and initial H_2 pressure of 5 MPa for 15 h. Then the gaseous products were trapped at −196°C and analysed by RGLC. In the similar run with $Os^{14}CH_x$, prepared from $^{14}C_6H_6$ with $\alpha = 1.12$, and C_5H_{12} ($\alpha = 0$) all alkanes from C_1 to C_5 were shown to contain ^{14}C by RGLC. The similar procedure was carried out with cyclo-$^{14}C_6H_{12}$ ($A = 1030$) and $OsCH_x$. The resulting A values were 435 for the mixture of C_1–C_6 alkanes and 650 for $OsCH_x$.

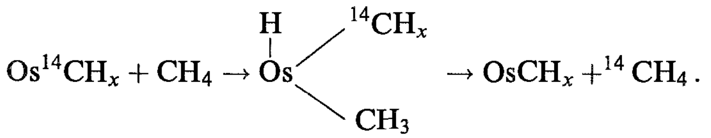
3. Results and discussion

First of all we have shown the possibility of applying the isotopic method for elucidation of the role of carbonaceous ligands in Os-LDC. Actually the composition of the Os-LDC, formed in standard conditions in alkanes or benzene, does not depend on the nature of the hydrocarbon used, reaction time and temperature (at least at temperatures $\leqslant 150$°C). The catalyst structure remains constant even after its reuse. According to EXAFS and elemental analysis data, the Os-LDC composition ranges from $OsC_{0.35}$ to $OsC_{0.48}$ (see table 1 in ref. [2]). Thus, one might have predicted that the ^{14}C labeling method would allow answering the question, whether carbonaceous ligands participate in the reactions, because the $^{14}C/^{12}C$ exchange that occurred was not due to increase of the carbon content in the ligand.

A priori the following most probable events could be proposed.

(1) Carbonaceous ligands do not participate in hydrocarbon reactions (no exchange).

(2) Carbonaceous ligands are exchanged with alkanes according to the known alkanolysis [7] or metathesis of σ-M–C bond mechanism [8] (exchange in the absence of H_2):



$$Os^{14}CH_x + CH_4 \rightarrow \overset{H}{Os}(^{14}CH_x)(CH_3) \rightarrow OsCH_x + {}^{14}CH_4 .$$

(3) Carbonaceous ligands take part in the reactions of saturated hydrocarbons in the presence of H_2.

Two routes are possible in the latter case.

(a) Carbonaceous ligands are hydrogenated by H_2 and this leads to a product desorption and production of vacant coordination sites on the metal atoms. Novel carbonaceous ligand formation proceeds with participation of hydrocarbons which are present in the reaction mixture. According to this scheme nonradioactive hydrocarbons formed in the course of ^{12}RH cracking in the presence of $Os^{14}CH_x$ will be diluted by ^{14}C-containing alkanes which are formed from $Os^{14}CH_x$ (and vice versa in cracking reactions of ^{14}RH in the presence of $Os^{12}CH_x$). The general scheme may be represented as follows:

$$Os_m \sum {}^{14}C_iH_x + C_nH_{2n+2} \xrightarrow{H_2} Os_m \sum {}^{12}C_iH_x + \underset{\text{alkanes}}{\sum ({}^{14}C_i + {}^{12}C_i) + \sum {}^{12}C_{n-i}} .$$

Here C_iH_x are all ligands in Os-LDC and, in principle, i can vary from 1 to n.

(b) In addition to a carbonaceous overlayer removal the reverse process of C–C bond formation proceeds to result in the $^{14}C/^{12}C$ exchange between $OsCH_x$ and alkanes,

$$Os^{14}CH_x + C_nH_{2n+n} \xrightarrow{H_2} Os^{12}CH_x + \underset{\text{alkanes}}{{}^{14}C_1 + {}^{14}C_2 + \ldots + {}^{14}C_n} .$$

The reversibility of C–C bond formation and cleavage on metal atoms may be considered as an evidence in favour of such assumption [9–12].

The experimental data are presented in table 1. It can be seen that the carbonaceous ligands of Os-LDC are substituted for carbon atoms of hydrocarbons in the course of hydrocracking of pentane and cyclohexane. The $^{14}C/^{12}C$ exchange takes place between CH_4 and $Os^{14}CH_x$ in the presence of H_2 and does not occur in its absence. A similar result was observed for Os-clusters of $OsC_{0.2}$ composition, which were formed in the following experiment: mild air oxidation of Os-LDC at 20°C, hydrogenation of dry oxidized catalyst at 150°C and $P_{H_2} = 0.5$ MPa for 15 h and hydrocracking of pentane on the resulted Os-system at 150°C and $P_{H_2} = 5$ MPa for 15 h. Thus, the prepared catalyst, containing less carbonaceous ligands than considered above, also exchanged its carbon for carbon atoms of cyclo-$^{14}C_6H_{12}$ and products of its cracking (table 1, values in parentheses). The catalyst composition also remained unaltered after the experiment.

Using the RGLC method we found that all alkanes formed in the course of hydrocracking of C_5H_{12} in the presence of $Os^{14}CH_x$ were radioactive (run No. 4 in table 1) and the ^{14}C content, being maximum in CH_4, decreased in the order

$$C_1 > C_2 > C_4 > C_3 > C_5 .$$

All the above experimental results may be represented by the following scheme:

Table 1

Radioactivity distribution on preparation and transformations of $OsCH_x$ under the action of hydrocarbons

Run[a]	Conditions of reaction $[H_2] : [RH] : [OsCH_x]$	Starting reagents and radioactivity A or α		Radioactivity of products A or α[b]	
1	2 : 1 : 0.02 periodical H_2 injection	$^{14}C_6H_6$	$A = 5864$	$^{14}C_6H_{12}$	$A = 5263$
		OsO_4		$Os^{14}CH_x$	$A = 468$
		H_2			
2	2 : 1 : 0.02	$^{14}C_6H_{12}$	$A = 1030(920)$[c]	$^{14}(C_1–C_6)$ alkanes	$A = 435(335$[c]$)$
		$OsCH_x$	$A = 0(0)$	$OsCH_x$	$A = 650(557$[c]$)$
		H_2			
3	5 : 1 : 0.05	C_5H_{12}	$A = 0$	$^{14}(C_1–C_5)$ alkanes	$A = 17$
		$Os^{14}CH_x$	$A = 465$	$Os^{14}CH_x$	$A = 5$
		H_2			
4	6 : 1 : 0.08	C_5H_{12}	$\alpha = 0$	CH_4	$\alpha = 0.09$
		$Os^{14}CH_x$	$\alpha = 1.12$[d]	C_2H_6	$\alpha = 0.02$
				C_3H_8	$\alpha = 0.003$
		H_2		C_4H_{10}	$\alpha = 0.016$
				C_5H_{12}	$\alpha = 0.002$
5	33 : 1 : 0.33	CH_4	$A = 0$	$^{14}CH_4$	$A = 82$
		$Os^{14}CH_x$	$A = 650$	$Os^{14}CH_x$	
		H_2			
6	0 : 1 : 0.33	CH_4	$A = 0$	CH_4	$A = 2$
		$Os^{14}CH_x$	$A = 650$	$Os^{14}CH_x$	

[a] Run 1: 20°C, 3 days, runs 2–6: 150°C, 15 h. In runs 1–4 initial $P_{H_2} = 5$ MPa.

[b] A is the specific radioactivity in imp.min^{-1} mg ($BaCO_3$) determined after the sample combustion to CO_2 with following conversion into $BaCO_3$. α is the specific radioactivity measured as the ratio of RGLC/GLC peaks.

[c] For Os-LDC of the $OsC_{0.2}$ composition.

[d] $\alpha = 1.12$ for $^{14}C_6H_6$ from which $Os^{14}CH_x$ was obtained.

$$Os^{14}CH_x + CH_4 \xrightarrow{H_2} OsCH_x + {}^{14}CH_4\,,$$

$$Os^{14}CH_xC_nH_{2n+2} \xrightarrow{H_2} OsCH_x + {}^{14}(C_1 + C_2 + ... + C_n)\text{ alkanes}\,,$$

$$OsCH_x + {}^{14}C_6H_{12} \xrightarrow{H_2} Os^{14}CH_x + (C_1 + C_2 + ... + C_6)\text{ alkanes}\,,$$

$$Os^{14}CH_x + CH_4 \nrightarrow OsCH_x + {}^{14}CH_4\,.$$

The experimental data agree well with the route (3), but the choice between alternative routes (3a) and (3b) is difficult.

Thus the carbonaceous ligands of Os-LDC are experimentally proved to take part in reactions of alkanes and cycloalkanes in the presence of H_2.

The role of carbonaceous ligands in hydrocarbon reactions has been the subject of many investigations [13–17]. All the authors cited agree that metal catalyzed hydrocarbon reactions such as hydrogenolysis and isomerization of alkanes, H/D exchange of alkanes with D_2, the ring opening reaction of cyclopropane and methylcyclopentane, reforming reactions of alkanes etc. occur exclusively on bare metal atoms and it is precisely these carbonaceous ligands that are the main cause of deactivation of catalysts. The results of studies of carbonaceous ligands formed on the Pt(111) surface in the course of hydrogenation of olefins allowed Somorjai to state that "the strongly adsorbed organometallic species on the surface play only secondary or peripheral roles in catalytic organic reactions" [13]. In full agreement with this author Engstrom [14] concluded that carbonaceous species on the Ir single crystal do not participate in alkane hydrocracking, but play a role of "spectators".

Initially formed hydrogen-rich carbonaceous species were shown to serve in olefin hydrogenation reactions as a "ferryman" by transferring hydrogen to the second layer to be hydrogenated [16,17]. It was noted that these species might provide hydrogen atoms for product desorption (resulting in appearance of vacant sites) and play a significant role in lubrication [13].

The results of our work show, however, that the role of carbonaceous ligands in hydrocarbon reactions can be more important. In contrast to the other metallic catalysts, wherein carbonaceous species block active centres, in the Os-LDC these ligands are chemically labile and perform at least two functions: stabilization of clusters to sintering and preservation of active centres. These LDC with reactive carbonaceous ligands can be considered as true organometallic compounds. However, they differ from classical molecular metal clusters with weakly bonded ligands mainly by the non-homogeneity of composition (representing mixtures of cluster species) and insolubility in organic media.

Small clusters with carbonaceous ligands, which exhibit both good stabilizing effect and high chemical reactivity, are of a great interest as effective catalysts. The following factors would probably facilitate the formation of these LDC: a high activity of the M–C bond and the ability to catalyze reactions under mild conditions minimizing the formation of inactive carbon forms bonded to metal atoms.

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