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Osmium ligand deficient clusters as catalysts for liquid phase hydrocarbon transformations

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Reduction of OsO_4 by molecular hydrogen in alkane (cycloalkane) or benzene media at 20–150°C yields small osmium clusters of the $Os_1C_{0.34-0.48}H_{0-0.6}$ composition with a specific surface area of 34–46 m^2/g. The systems obtained are shown to be ligand deficient osmium clusters (LDC) of 7–16 Å in diameter, stabilized by a small amount of carbonaceous ligands with Os–Os = 2.68–1.70 Å and Os–C = 2.11–2.19 Å. The characteristics of these chemically prepared Os-LDC are similar to those of Ni- and Co-LDC, prepared by a vapour phase synthesis. The novel Os-LDC effectively catalyze hydrogenolysis of alkanes and cycloalkanes at 100–150°C and initial H_2 pressure of 5 MPa, hydrogenation of cyclopentadiene and arenes 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.

Keywords: Osmium ligand deficient metal clusters; chemical synthesis and catalytic properties of small clusters; hydrocracking of paraffins; hydrogenation of arenes; H/D exchange; CO_2 methanation

1. Introduction

Ensembles of 20–150 metal atoms, stabilized by a low number of ligands, occupy an intermediate position between bulk metals and classical molecular clusters, differing from both of them by a high concentration of surface metal atoms with low coordination numbers. For this reason such clusters, named by us "ligand deficient clusters" (LDC)[#1], are of considerable interest for catalysis. Usually such catalytic systems are prepared by a vapour phase synthesis, requiring special high vacuum equipment. For LDC of heavy metals, representing a special interest

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[#1] Other terms such as SMAD (according to the preparation method, namely the solvated metal atom deposition technique), ultradispersed metals, small "bare" clusters, ultrafine particles etc. are also used [1–3].

for catalysis, resistive heating techniques are very limited in scale because of a lack of materials which can survive temperatures needed for vaporization. In addition pure metals used as starting materials are often unavailable. These factors restrict the wide application of the method.

Reported chemical approaches for the LDC preparation are based on using highly polar media or/and polymers to avoid agglomeration [4–7]. At the same time clusters obtained under these conditions contain very tightly bound ligands and therefore they are not active in alkane cracking, arene hydrogenation and other reactions [#2]. For example the very small Ni-LDC of 5–15 Å in diameter prepared by vapour phase synthesis in THF are not active for arene hydrogenation, in contrast to Ni-LDC prepared in alkanes [9]. Pyrolysis of the latter yields mainly methane but pyrolysis of Ni-LDC prepared in THF affords a mixture of products, viz. THF, butanol, furan, butanal, ethylene etc. [10]. Small Os-LDC, prepared by reduction of OsO_4 by methanol at 64°C in the presence of polyvinylpyrrolidone (PVP) as a stabilizing agent, are not active for arene hydrogenation. We have also shown that the reported reduction of metal chlorides MCl_n by RLi ($M = Pd$, Ni, Ru, $R = Bu$, Cp) at 20°C in ether or THF to small metal clusters [4] does not lead to active catalysts for paraffin hydrocracking. Thus LDC, formed in hydrocarbon media, seem to be more active than clusters obtained in polar solvents or in the presence of polymers (at least for such reactions as hydrogenation of arenes and hydrocracking of paraffins).

To the best of our knowledge the chemical syntheses of LDC in hydrocarbons or arenes without stabilizators have not been reported earlier.

Two questions were the focus of the present work. Is it possible to prepare the Os-LDC in non-polar hydrocarbon media without any stabilizing additive? Will this method lead to clusters active in alkane hydrocracking?

We attempted to prepare the Os-LDC by homogeneous reduction of OsO_4 with H_2 in solutions of saturated or aromatic hydrocarbons. It should be stressed that these conditions for the preparation of catalysts are quite close to those for hydrocracking of alkanes. Such factors as lower reduction temperature, use of dilute solutions and absence of any solvents and reductants capable of deactivation of developing clusters should clearly favour the preparation of LDC.

2. Experimental

All operations with catalysts, including sampling for elemental analysis and spectra measurements were performed in an atmosphere of purified Ar. Hydrocar-

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[#2] However, such methods are very fruitful for synthesizing small clusters or colloids possessing a high activity for certain reactions [4–8].

bons were purified by standard procedures, then dried, refluxed and distilled over $LiAlH_4$ before use.

Osmium tetraoxide (Russian "chemical pure" grade) was used without purification. Diisobutylaluminium hydride (DIBAH) was vacuum distilled under Ar immediately before use.

GLC was performed with a Chrom-5 chromatograph. Gaseous products were analyzed on a packed 250 × 0.3 cm PAR-2 stainless steel column (temperature program 25–180°C, 15°C/min). Liquid products were analyzed using a 1 m × 0.22 mm OV-101 glass capillary column (temperature program 30–150°C, 4°C/min). GLC-MS analyses were carried out with a VG-7070E instrument (70 eV, 150°C). EXAFS spectra of Os-LDC suspensions in absolute Apiezon-Fett M were measured in air immediately after preparation. X-ray powder diffraction (XRPD) patterns of samples, prepared under argon in silicone grease or in a mixture of polyalkyladamantanes, obtained by our method [11], were measured with a Guinier camera.

Before all analytical procedures, catalyst samples were thoroughly washed with pentane and dried in vacuo (10^{-1}–10^{-2} Torr) for 1.5–2 h. The specific surface area of catalysts was measured by thermal desorption of Ar and calculated by the BET method using the Temkin equation [12]. Os-LDC samples were prepared by the general method, previously reported by us [13].

Os-LDC preparation (general method). A suspension of OsO_4 (0.127 g, 0.5 mmol) in 500–100 mmol of saturated hydrocarbon was heated for 3–15 h in a 50 ml stainless steel autoclave at 100–150°C and initial H_2 pressure of 5 MPa. The gaseous products from the autoclave, cooled to room temperature, were condensed in a cooled trap (−196°C) and analyzed by GLC. The liquid products were distilled from the autoclave and analyzed by GLC after addition of an internal standard. The catalyst was stored in the autoclave under an Ar atmosphere. Hydrocracking of alkanes or cycloalkanes, used as solvents, was observed in the process of Os-LDC formation.

Hydrogenolysis of alkanes and cycloalkanes. A freshly distilled hydrocarbon was added under argon in the autoclave to a catalyst carefully dried in vacuo, then H_2 was introduced, and the mixture was heated at the selected temperature for 3–15 h. Cycles could be repeated after distilling of the volatile products and adding new portions of hydrocarbons.

Catalyst formation in saturated hydrocarbon on reduction of OsO_4 by DIBAH under H_2 pressure. A solution of DIBAH in saturated hydrocarbon was placed in an autoclave containing a thin-walled sealed glass ampoule with a sample of OsO_4. Then H_2 was introduced. The ampoule was broken and the autoclave contents were stored overnight and then heated at 180°C for 15 h. Product analysis and repeated use of the catalytic system were carried out as described for the previous experiment.

Catalyst formation and hydrogenation of benzene and toluene. A solution of 0.127 g (0.5 mmol) of OsO_4 in 25–50 mmol of benzene or toluene was shaken in a steel autoclave at 20°C and $P_{H_2} = 3$ MPa for 3–4 days (the induction period is one day), periodically adjusting the H_2 pressure to 3 MPa. After hydrogen absorption ceased, cyclohexane and benzene (methylcyclohexane and toluene) were distilled from the autoclave and a new portion of benzene (toluene) was added to the remaining catalyst under an Ar atmosphere. Heating occurred and the hydrogenation proceeded even more rapidly (at molar ratio ArH : Os = 100 : 1 with vigorous stirring hydrogenation was completed in 5 min to 3 h). Repetition of this cycle once or twice produced a catalyst capable of hydrogenation of benzene at 20°C and $P_{H_2} = 0.1$ MPa.

Hydrogenation of cyclopentadiene. Freshly distilled cyclopentadiene (80 ml) was added to 1 g of catalyst formed in benzene and the mixture was stirred under H_2 pressure (2.5 MPa) (Caution! Very exothermic!) with cooling of the autoclave from outside with a stream of air. After 1 h, cyclopentane was distilled from the autoclave. Yield 95–98%.

CH_4/D_2 exchange over Os-LDC. A mixture of CH_4 and D_2 was heated in an autoclave over the carefully dried (in vacuo) sample of Os-LDC under selected conditions. After cooling the gaseous mixture was collected and analyzed by MS.

Methanation of CO_2. A mixture of CO_2 and H_2 (1 : 3–4.5) was heated in an autoclave at 150 or 180°C over previously prepared Os-LDC. The yields of CH_4 per 1 mol of catalyst were 3 and 10 mol respectively.

3. Results and discussion

Reduction of OsO_4 by molecular hydrogen in alkanes (C_5–C_{17}), cycloalkanes (C_5–C_6) or arenes (C_6H_6, $C_6H_5CH_3$) at 100–150°C for 3–15 h or at 20°C for 3 days (initial $P_{H_2} = 5$ MPa) yields the pyrophoric black or gray-black powders insoluble in ordinary organic solvents. According to elemental analysis these osmium powders contain a significant quantity of carbon (table 1). The analytical data are consistent with the empirical formula given in the equation

$$OsO_4 + 4H_2 \xrightarrow[-4H_2O]{} \text{“Os”} \xrightarrow{RH} Os_1C_{0.34-0.68}H_{0-0.6}\,.$$

The composition of osmium samples prepared in hexane at 150°C and in benzene at 20°C remains constant and does not change after reuse. According to elemental analysis data the composition ranges from $OsC_{0.34}$ to $OsC_{0.48}$. However, the samples prepared in toluene contain a markedly greater amount of carbon (table 1).

The osmium systems were studied by XRPD, EXAFS, XANES, electron microscopy and by chemical reactions [13,14].

The XRPD patterns have only one very diffuse (111) line with $d = 2.08$ Å instead of four main lines of metallic osmium. EXAFS and XANES data show the

Table 1
Elemental analysis of Os-systems

Formation conditions			Operations before analysis	Composition (%)			Empirical formula
RH	OsO_4 : RH (mol)	T^a(°C)		Os	C	H^b	
n-C_6H_{14}	1 : 50	150		97.4	2.6	0	$OsC_{0.42}$
				97.6	2.9	0	$OsC_{0.47}$
n-C_6H_{14}	1 : 50	150	hydrogenolysis of $C_{17}H_{36}$	96.8	2.3	0.2	$OsC_{0.38}H_{0.4}$
				97.5	2.5	0.2	$OsC_{0.41}H_{0.4}$
C_6H_6	1 : 50	20	(1) 4-fold hydrogenation of C_6H_6 at $P_{H_2} = 3$ MPa	91.1	2.0	0.3	$OsC_{0.35}H_{0.6}$
			(2) single hydrogenation of C_6H_6 at $P_{H_2} = 0.1$ MPa	93.2	2.5	0.3	$OsC_{0.42}H_{0.6}$
$C_6H_5CH_3$	1 : 100	20	(1) 3-fold hydrogenation of C_6H_6 at $P_{H_2} = 0.1$ MPa	90.3	3.8	0.3^c	$OsC_{0.67}H_{0.6}$
			(2) single hydrogenation of C_6H_6 at $P_{H_2} = 0.1$ MPa	90.6	3.9	0.3^c	$OsC_{0.68}H_{0.63}$

[a] Reaction time for experiments carried out at 150 and 20°C are 15 and 3 days respectively.
[b] Accuracy is ±0.3%.
[c] According to X-ray fluorescence analysis contains traces of iron.

systems studied to be actually the small osmium clusters with particle diameter of 7–12 Å (when prepared in benzene at 20°C) and 12–16 Å (at 150°C) with the Os–Os distance of 2.68–2.70 Å. Each Os atom is bonded to 0.32–0.39 carbon atoms at Os–C = 2.11–2.19 Å [14,15].

Preliminary transmission electron microscopy data for the samples of Os systems, prepared at 20°C, show the presence of 10 Å particles together with larger species up to 100 Å in diameter. Taking into account EXAFS data one can suggest that the latter have been produced under the action of high energy electrons in the course of measurements. This effect has been noted previously for palladium particles as well as for supported metals [8,16].

Hydrogenation of the dry catalysts at 150°C and $P_{H_2} = 0.1$–0.5 MPa produces CH_4 in 17% yield (based on Os), while the reaction with D_2 yields a mixture of deuteriomethanes in the ratio $CD_4 : CD_3H : CH_2D_2 : CH_3D = 1.1 : 1.0 : 1.5 : 0.7$.

According to EXAFS spectra careful oxidation of the pyrophoric clusters by an air–argon mixture for 2 h does not destroy the cluster structure, although the size of 10 Å clusters is increased approximately twice [15].

The characteristics of the Os–LDC prepared chemically are similar to the earlier reported Ni- and Co-LDC obtained by a vapour phase synthesis (SMAD) (table 2). In all cases methane is the only product of LDC hydrogenation.

Table 2
Comparison of Os-LDC (chemical synthesis) with Ni- and Co-LDC (vapour phase synthesis)

Metal	Empirical formula	Specific surface area (m^2/g)	Particle size (Å)
Os (20°C, benzene)	$OsC_{0.34-0.42}H_{0.6}$	–	7–12
Os (20°C, toluene)	$OsC_{0.67}H_{0.6}$	34	–
Os (150°C, hexane)	$OsC_{0.38-0.47}H_{0.4}$	46	12–16
Ni [3]	$NiC_{0.1-0.5}H_{0.3-1.5}$	37–70	25–36
Co [3]	$CoC_{0.25}H_{0.5}$	–	18–21

The Os-LDC were shown to be effective catalysts for alkane and cycloalkane hydrocracking at 100–150°C and initial H_2 pressure of 5 MPa. Under these conditions one mole of catalyst converts hundreds of moles of hydrocarbon in 5–15 h. The catalysts can be used repeatedly without loss of activity. Careful oxidation of the pyrophoric catalyst by an air–argon mixture for 2 h does not reduce its activity. Table 3 shows that hydrogenolysis of *n*-alkanes proceeds effectively at 120°C. Using the Os-catalyst prepared in toluene 89% of the pentane is converted (89 mol/mol Cat) in 15 h. The products of the C_nH_{2n+2} ($n = 5, 6, 8, 17$) conversion at 120–150°C for 15 h are a series of lower, exclusively linear alkanes from C_1 to C_{n-1} of which methane, ethane and propane comprise 80–97%. Cyclopentane and methylcyclopentane undergo hydrogenolysis to a great extent even at 100°C (under these conditions the C_5H_{10} conversion is 14 mol/mol Cat in 15 h). At 120°C hydrogenolysis of cyclopentane occurs effectively and rather selectively: in 15 h the conversion is 94% and *n*-pentane is formed in 90% yield; at 150°C the cyclopentane conversion is ca. 30 NOT/h (table 3). In methylcyclopentane selective ring opening occurs at 100°C with a rupture of the least shielded bonds and formation of 2-methylpentane (c) and 3-methylpentane (d):

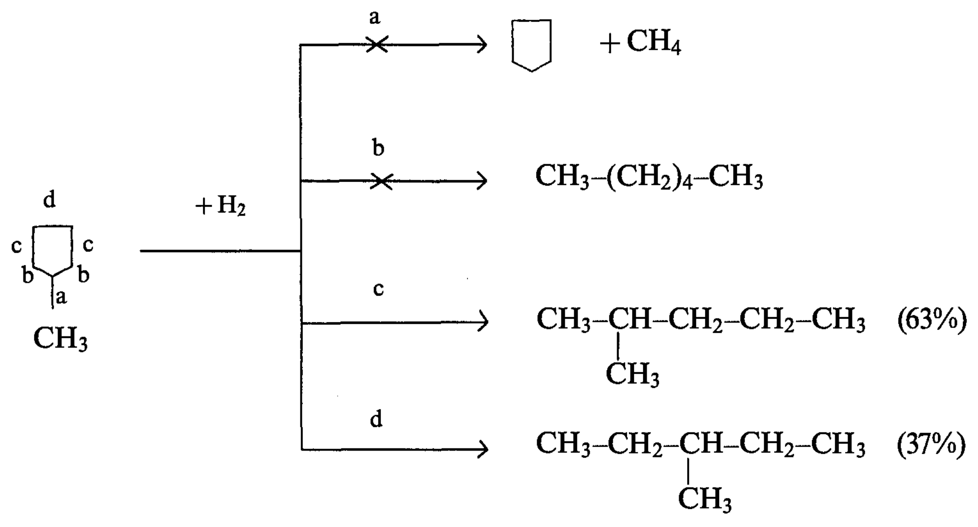


Table 3

Hydrogenolysis of alkanes and cycloalkanes on Os-LDC in liquid phase (P_{H_2} = 5 MPa, 15 h)

RH	Catalyst[1]	RH : Cat (mol)	T (°C)	RH (%)	Conversion (mol RH/mol Cat)	C_nH_{2n+2} products (mol/mol reacted RH)				
						C_1	C_2	C_3	C_4	C_5
c-C_5H_{10}	Os^a	100 : 1	100	14	14	0.01	0.01	0.01	0.001	0.85
c-C_5H_{10}	Os^a	100 : 1	120	57	57	0.21	0.04	0.01	0.04	0.91
c-C_5H_{10}	Os^a	50 : 1	120	94	47	0.22	0.09	0.07	0.04	0.88
c-C_5H_{10}	Os-black	50 : 1	120	0	0	–	–	–	–	–
c-C_5H_{10}	Os^a	200 : 1	150	99	198	0.72	0.33	0.20	0.10	0.45
c-C_5H_{10}	Os^b	50 : 1	150	90	45	0.98	0.38	0.22	0.09	0.28
c-C_5H_{10}	Os-black	50 : 1	180	7	3.5	0.07	0.02	0.01	0.01	0.80
c-C_5H_{10}	Os^c	250 : 1	150	77[2]	192	–	–	–	–	–
c-$C_5H_9CH_3$[3]	Os^a	50 : 1	100	12	6	–	–	–	–	–
c-C_6H_{12}	Os^a	200 : 1	150	89	178	0.44	0.24	0.14	0.11	0.10[4]
n-C_5H_{12}	Os^d	100 : 1	120	32	32	3.07	0.11	0.04	0.09	–
n-C_5H_{12}	Os^c	100 : 1	120	89	89	2.20	0.71	0.31	0.06	–
n-C_5H_{12}	Os^a	100 : 1	150	61	61	3.46	0.47	0.17	0.07	–
n-C_6H_{14}	Os^d	100 : 1	150	48	48	3.06	0.44	0.11	0.06	0.07
n-C_6H_{14}	Os^a	200 : 1	150	60	120	3.24	0.50	0.11	0.04	0.10
n-C_8H_{18}	Os^a	200 : 1	150	39	78	0.41	0.38	0.22	0.13	0.8[5]
n-$C_{17}H_{36}$	Os^a	50 : 1	150	91	46	2.80	0.53	0.28	0.16	0.14[6]

[1] Os^a is formed in alkanes or cycloalkanes on heating, Os^b is formed with i-Bu_2AlH at 180°C and molar ratio OsO_4: i-Bu_2AlH = 1 : 5.6, Os^c in toluene at 20°C, Os^d in pentane at 20°C.

[2] For 6 h.

[3] The main products are 2- and 3-methylpentane (0.54 and 0.31 mol).

[4] And 0.25 of C_6.

[5] And 0.22 of C_6 and 0.12 of C_7.

[6] And $C_6 = 0.11$, $C_7 = 0.09$, $C_8 = 0.07$, $C_9 = 0.06$, $C_{10} = 0.05$, $C_{11} = C_{12} = 0.04$, $C_{13} = C_{14} = C_{15} = 0.03$, $C_{16} = 0.02$.

The inertness of 1,3-dimethyladamantane at 200°C ($P_{H_2} = 5$ MPa, 15 h) also indicates the resistance of shielded C–C bonds to hydrocracking.

On the other hand, at 150°C hydrogenolysis of cycloalkanes does not proceed selectively. This is associated with the facile hydrocracking of the alkanes formed under these conditions. As a result, the fraction of ring-opening products decreases and the content of CH_4, C_2H_6 and C_3H_8 increases. Thus, cyclohexane at 150°C effectively undergoes hydrocracking (89% conversion in 15 h, 178 mol/mol Cat) and forms C_1–C_6 alkanes, among which methane, ethane and propane predominate (table 3).

Metallic osmium [17–19] belongs to a group of active catalysts for alkane and cycloalkane hydrogenolysis. However, Os-black, a traditional catalyst for liquid phase paraffin hydrocracking and chosen by us as a reference catalyst, shows a markedly lower activity than the Os-LDC. As shown in table 3, the Os-black, prepared according to ref. [20], is completely inactive at 120°C. Its activity at 180°C is essentially less than that of the Os-LDC prepared at 100°C. Spongy osmium is even less active.

The Os-LDC catalyze H/D exchange between CH_4 and D_2. The reaction proceeds very slowly even at 50°C. At 100–120°C the exchange is of a multiple character and M is 1.7 at 100°C and 2.62 at 120°C (M = average number of D atoms in molecule, i.e. $M = \sum_{i=1}^{4} id_i$). The data obtained are presented in table 4, which shows that the deuteriomethane concentration at 100°C displays maxima at monodeuterio- and perdeuteriomethanes. This result together with the multiple character of the H/D exchange at 100 and 120°C is in good agreement with previous studies on the reaction of methane and other alkanes with deuterium over metals (as evaporated films, supported catalysts or single crystal surfaces) [21–28]. Therefore the scheme, suggested by Kemball [25] and later confirmed by Zaera [28] also can be proposed for the reaction of CH_4 with D_2 in the presence of Os-LDC. It involves an initial dissociative chemisorption of methane on Os atoms. The methyl groups formed then react by two competing pathways, undergoing rehydrogenation to methane and dehydro-

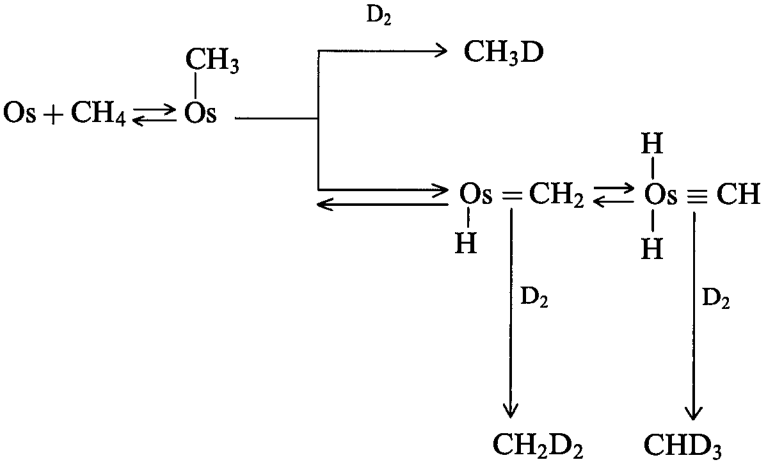


Table 4
Composition of deuteriomethanes in the reaction of CH_4 and D_2 catalyzed by Os-LDC ($CH_4 : D_2 : Os = 50 : 112 : 1$; 15 h)

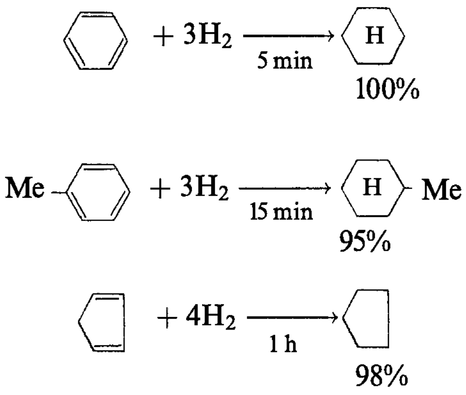
T (°C)	d_i (%) ($d_i / \sum id_i$)				D (%)	M
	d_1	d_2	d_3	d_4		
100	10.5 (0.68)	1.1 (0.07)	1.3 (0.08)	2.5 (0.16)	15.4	1.7
120	8.8 (0.17)	14.4 (0.29)	14.4 (0.29)	12.7 (0.25)	50.3	2.6

genation to methylene and finally to methylidyne. The first pathway results in monodeuteriomethane and the second one leads to multideuteriomethane:

The formation of methyl, methylene and methylidyne groups on metals was experimentally proved earlier [29–31].

The activation energies of the direct M–CH_3 hydrogenation and of the M–CH_3 to M$=CH_2$ transformation were determined by Zaera [28] for Pt(111) to be 170 ± 1.0 and 6.5 ± 1.0 kcal/mol respectively.

At 20°C Os-LDC catalyze hydrogenation of benzene, toluene, selective hydrogenation of cyclopentadiene[#3] to cyclopentane and at 150–180°C methanation of



$$CO_2 + 4H_2 \xrightarrow[10\,h]{150\text{–}180°C} CH_4 + 2H_2O$$

3–10 mol/mol Cat

[#3] The reaction with cyclopentadiene was carried out without optimization of conditions.

CO_2. The reactions presented below were carried out at $P_{H_2} = 3$ MPa (for hydrocarbons) and at the ratio $CO_2 : H_2 = 1 : (3–4.5)$ (for CO_2):

The Os-LDC activity (in mmol g^{-1} min^{-1}) in hydrogenation of benzene is 1.8 ($P_{H_2} = 0.1$ MPa) and 53 ($P_{H_2} = 2$ MPa) and of toluene is 18 ($P_{H_2} = 2$ MPa). Unfortunately, data for the Os-LDC prepared chemically or by the SMAD techniques were not published before. The activity of Rh clusters, prepared by the vapour phase synthesis, in toluene hydrogenation at 20°C and $P_{H_2} = 0.1$ MPa is 0.29 mmol g^{-1} min^{-1} (calculated by us on the basis of ref. [32]).

Thus, the small ligand deficient osmium clusters of 7–16 Å in diameter can be prepared chemically in non-polar hydrocarbon media without any polymer stabilizer. These Os-LDC are good catalysts for hydrocarbon transformations under rather mild conditions.

The important question is whether the "hydrocarbon method" of Os-LDC synthesis has an advantage over the previously reported chemical methods for preparation of active catalysts for hydrocarbon transformations. In order to answer this question we studied the Os-systems prepared by us from OsO_4 by various methods in polar media under argon.

Reduction of OsO_4 at 20°C for 3 days by methanol and by methanol in the presence of H_2 ($P_{H_2} = 0.1$ MPa), as well as reduction at 64°C for 4 h by methanol or methanol in the presence of PVP (under the Hirai conditions [6]), were studied. According to EXAFS spectra [15] all Os-systems formed are composed of very small metal clusters of 5–10 Å in diameter with very bulky ligand cover changeable in dependence on preparation conditions. In the presence of H_2 larger clusters were formed. The pyrophoric 5 Å clusters of the $Os_2CH_2O_2$ composition formed in methanol at 64°C were shown by the XRPD patterns to be X-ray amorphous. Preliminary transmission electron microscopy data indicated the presence of particles from 50 to 150 Å in size. Perhaps the latter are due to coalescence of the initial microcrystallites into agglomerates under the electron beam. In contrast to the abovementioned Os-LDC these Os clusters did not catalyze benzene hydrogenation at 20°C and $P_{H_2} = 3$ MPa. On treatment of these 5 Å Os clusters with H_2 at 150°C in paraffin media their ligand cover seemed to change and they were transformed into 10 Å clusters. The latter were shown to catalyze alkane hydrocracking at 120°C and $P_{H_2} = 5$ MPa.

The small Os clusters prepared in the presence of PVP were completely nonactive for benzene hydrogenation (20°C, $P_{H_2} = 3$ MPa) as well as for pentane hydrocracking (150°C, $P_{H_2} = 5$ MPa). The retreatment of these systems by H_2 in hydrocarbon media at 150°C did not lead to activity.

4. Conclusions

Small (7–16 Å) osmium LDC can be prepared using non-polar hydrocarbon media. Such Os-LDC are good catalysts for hydrocarbon transformations under mild conditions (hydrocracking of paraffins, H/D exchange between CH_4 and D_2, hydrogenation of arenes and olefins). This "hydrocarbon" route to synthesis of the active Os-LDC has a distinct advantage over the earlier reported methods based on using polar solvents and polymers.

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