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OSMIUM LIQUID-PHASE CATALYSTS FOR HYDROGENOLYSIS OF SATURATED HYDROCARBONS AND HYDROGENATION OF ARENES

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Reduction of OsO_4 by molecular hydrogen in alkane (cycloalkane) or benzene (toluene) solution produces small-ligand clusters of osmium of composition $Os_{1.5-2.5}CH_{0-2}$ with a particle size 10-40 Å and a specific surface area of 34-46 m^2/g. Hydrogenation of dry catalyst produces methane. The small-ligand osmium clusters obtained effectively catalyze hydrogenolysis of alkanes and cycloalkanes at 100-150°C and P_{H_2} = 5 MPa and hydrogenation of benzene at 20°C and P_{H_2} = 0.1 MPa.

Catalytic cleavage of C–C bonds in saturated hydrocarbons under mild conditions is one of the most challenging problems of organic chemistry. In [1, 2], we found that systems based on rhenium complexes and organoaluminum compounds effectively catalyze hydrocracking of alkanes and cycloalkanes at 150-180°C and P_{H_2} = 5 MPa. Continuing the search for active catalysts, we focused attention on so-called "small-ligand" metal clusters (LMC), i.e., small metal clusters stabilized by a small number of ligands.* These systems are distinguished from bulk metals and molecular clusters by a large content of surface metal atoms with low coordination number.

LMC, forming strong M–C bonds, completely satisfy criteria for active hydrocracking of alkanes [2]. Therefore, they can be expected to be effective catalysts. Examples supporting this idea are given in [6]. The LMC are usually prepared by vapor-phase synthesis consisting of cocondensation of metal and organic compound vapors on a cooled surface [4, 5]. This method requires special equipment that seriously limits its widespread use.

We attempted to prepare LMC active catalysts by reducing OsO_4 with hydrogen in a solution of saturated or aromatic hydrocarbons (AH). Although the synthesis of LMC under liquid-phase conditions is reported in [7-9], a similar approach for preparing active catalysts for alkane hydrogenolysis has not yet been used. Such factors as lower reduction temperatures, dilute solutions, and a lack of solvents and reductants capable of forming complexes should clearly favor preparation of LMC.

Reduction of OsO_4 with hydrogen in alkanes (C_5-C_{17}) or cycloalkanes (C_5-C_6) at 100-150°C and P_{H_2} = 5 MPa for 3-15 h forms active catalysts for hydrogenolysis of saturated hydrocarbons and hydrogenation of AH. Formation of the active catalyst (in pentane, benzene, or toluene) at 20°C and P_{H_2} = 2-9 MPa takes 3 days. The catalysts formed at 20°C can be kept for a

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*Such terms as "bare" clusters, ultradispersed metals [3], and SMAD [4, 5] are also used.

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TABLE 1. Hydrogenolysis of Alkanes and Cycloalkanes on Liquid-phase Os-Catalysts (P_{H_2} = 5 MPa, 15 h)

RH	Catalyst*	RH:Cat (mole)	T, °C	H conversion		C_nH_{2n+2} products, mole/mole reacted RH				
				%	mole RH/ mole Cat	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^b	50 : 1	120	26	13	0,01	0,01	0,03	0.01	0,90
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^c	50 : 1	150	100	50	0,79	0,25	0,14	0,10	0,50
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-$C_5H_9CH_3$†	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
n-C_5H_{12}	Os^d	100 : 1	120	32	32	3,07	0,11	0,04	0,09	–
n-C_5H_{12}	Os^e	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
n-$C_{17}H_{36}$ ***	Os^a	50 : 1	150	91	46	2,80	0.53	0.28	0.16	0,14

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*Os^a is formed in alkanes or cycloalkanes with heating; Os^b, with i-Bu_2AlH at 180°C and mole ratio [OsO_4]:[i-Bu_2AlH] = 1:5.6; Os^c, in water at 150°C; Os^d, in pentane at 20°C; and Os^e, in toluene at 20°C.

†2-Methylpentane = 0.54, 3-methylpentane = 0.31.

‡C_6 = 0.25.

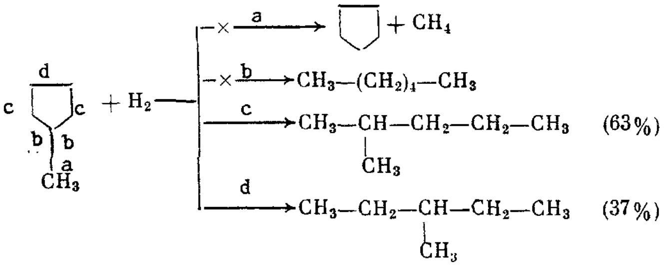
**C_6 = 0.22, C_7 = 0.12.

***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, G_{13} = C_{14} = C_{15} = 0.03, C_{16} = 0.02.

long time under Ar. However, storage of them in AH in the absence of H_2 can lead to irreversible poisoning.

Reduction of OsO_4 in alkane or toluene by hydrogen in the presence of diisobutylaluminum hydride (DIBAH) gives less active catalysts (Table 1). The complicated preparation and low activity of catalysts prepared with DIBAH make them less promising. Therefore, we did not study these catalysts further.

Besides the listed solvents, H_2O and CH_3COOH were also tried. Active catalyst is also formed in water at 150°C (P_{H_2} = 5 MPa) but not in CH_3COOH (Table 1). Hydrocracking of alkanes and cycloalkanes by the catalysts prepared occurs effectively at 100-150°C and P_{H_2} = 5 MPa. Under these conditions, one mole of catalyst converts 100 moles of hydrocarbon after 5-15 h. The catalyst can be used repeatedly without loss of activity. Careful oxidation of the pyrophoric catalyst by an air—argon mixture for 2 h did not reduce its activity. Table 1 shows that hydrogenolysis of n-alkanes proceeds effectively at 120°C. Pentane is 89% converted (89 mole/mole Cat) after 15 h using the Os-catalyst formed in toluene. The conversion products C_nH_{2n+2} (n = 5, 6, 8, 17) at 120-150°C after 15 h are a complete array of lower alkanes from C_1 to C_{n-1}, of which methane, ethane, and propane comprise 80-97%. Exclusively linear alkanes are formed. Cyclopentane (CPA) and methylcyclopentane (MCPA) undergo hydrogenolysis to a great extent even at 100°C (under these conditions, C_5H_{10} conversion after 15 h is 14 mole/mole Cat). At 120°C, hydrogenolysis of CPA occurs effectively and rather selectively. Starting C_5H_{10} is 94% converted after 15 h and n-pentane is formed in 90% yield (Table 1). In MCPA, selective opening of the ring occurs at 100°C with rupture of the least shielded bonds and formation of 2-methylpentane (c) and 3-methylpentane (d)



The inertness observed by us of 1,3-dimethyladamantane at 200°C (P_{H_2} = 5 MPa, 15 h) toward the catalysts synthesized also indicates passivity of shielded C—C bonds to hydrocracking.

At 150°C, hydrogenolysis of cycloalkanes does not occur 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 after 15 h, 178 mole/mole Cat) and forms C_1-C_6 alkanes, among which the largest fraction contains methane, ethane, and n-hexane (Table 1).

Metallic osmium [10-13] is one of a number of active hydrogenolysis catalysts for alkanes and cycloalkanes. Thus, n-hexane, n-pentane, and n-butane in a quantity of 5-13% are found in the catalyzate on gas-phase hydrocracking of cyclohexane on Os/C catalyst at 150-200°C and P_{H_2} = 0.1 MPa [10]. Catalysts prepared by supporting osmium carbonyls on Al_2O_3 exhibit high activity for hydrogenolysis of ethane at 140-400°C [13]. Moreover, supported catalysts actively carrying out hydrogenolysis in the vapor phase can be inactive in the liquid phase [6]. Therefore, Os-black, a traditional catalyst for the liquid-phase hydrocracking of saturated hydrocarbons, may serve as the reference catalyst as obtained in [14]. As seen in Table 1, the latter is completely inactive at 120°C. Its activity at 180°C is markedly less than that of the catalyst prepared by us at 100°C. Mossy osmium is even less active.

The osmium catalysts prepared catalyze hydrogenation of benzene and toluene at 20°C. Their activity in hydrogenation of benzene is 1.8 mmole·g^{-1}·min^{-1} (P_{H_2} = 0.1 MPa) and >53 mmole·g^{-1}·min^{-1} (P_{H_2} = 2 MPa) and of toluene, 18 mmole g^{-1}·min^{-1} (P_{H_2} = 2 MPa). The activity of Rh prepared by vapor-phase synthesis in hydrogenation of toluene at 20°C and 0.1 MPa is 0.29 mmole/g·min.* Unfortunately, data for LMC of osmium do not appear in the literature. As expected, these catalysts effectively catalyze selective hydrogenation of cyclopentadiene to CPA. This was used in the present work for preparation of the latter.

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*Calculated based on the data of [15].

TABLE 2. Elemental Analysis of Os-Catalysts

Formation conditions			Use before analysis	Composition, %		
RH	OsO_4:RH (mole)	T, °C		Os	C	H *
n-C_6H_{14}	1 : 50	150		97.4–97.6	2.6–2.9	0
n-C_6H_{14}	1 : 50	150	Hydrogenolysis of $C_{17}H_{36}$	96.8–97.5	2.3–2.5	0.2
C_6H_6	1 : 50	20	Hydrogenation of C_6H_6 at 3 MPa H_2 4 times, then at 0.1 MPa H_2 once; [Os]:[C_6H_6] = 1:50, 20°C	91.1–93.2	2.0–2.5	0.3
C_6H_5–CH_3	1 : 100	20	Hydrogenation of C_6H_6 at 3 MPa H_2 3 times, then at 0.1 MPa H_2 once; [Os]:[C_6H_6] = 1:100, 20°C	90.3–90.6	3.8–3.9	0.3 **

*Uncertainty of H ±0.3%.

**Contains traces of iron according to x-ray fluorescence analysis.

TABLE 3. Properties of Os-Catalysts and LMC of Ni and Co [5]

Metal	Empirical formula	S_{sp}, m^2/g	Particle size, Å
Os (20°, toluene)	$Os_{1.5}CH_{0-2}$	34	10–20
Os (150°)	$Os_{2.3-2.5}CH_{0-2}$	46	20–40
Ni	$Ni_{2-9}CH_{2-3}$	37–70	25–36
Co	Co_4CH_2	–	18–21

The Os-catalysts obtained are pyrophoric black or gray-black powders that are insoluble in organic solvents. According to elemental analysis, they contain a significant quantity of C (Table 2). Their empirical formula is consistent with $Os_{1.5-2.5}C_{0-2}$. Catalysts prepared at lower temperatures contain more C.

X-ray phase analysis indicates that the only crystalline phase in the catalysts is metallic osmium. The EXAFS* spectra are consistent with the LMC having particle size 10-20 Å for samples synthesized at 20°C and 20-40 Å for those prepared at 150°C (Table 3). Table 3 shows that the Os-catalysts are similar to LMC of Ni and Co.

Hydrogenation of dry catalyst on heating in an autoclave or in a flow system produces methane. Deuteration of dry catalyst produces a mixture of products in the following ratios CD_4:CD_3H:CH_2D_2:CH_3D = 1.1:1.0:1.5:0.7. Apparently these data are consistent with CH_x groups, where x = 0-3, bonded to Os in the catalysts studied.

EXPERIMENTAL

All operations with catalysts, including taking samples for analysis, were performed in an atmosphere of purified Ar. Pure dry hydrocarbons were used for catalyst formation. Alkanes, cycloalkanes, and arenes were refluxed and distilled over lithium aluminum hydride under Ar immediately before use. Osmium tetroxide (TU 6-09-05-118-74) was used as received. DIBAH was vacuum distilled and stored under Ar.

GLC was performed on a Chrom-5 chromatograph. Gaseous products were analyzed on a packed PAR-2 column of l = 2.5 m and diameter 3 mm using a temperature program from −25-180°C at a rate of 15 K/min. Liquid products were analyzed on an OV-101 glass capillary column of l = 1 m and diameter 0.22 mm from 30-150°C at a rate of 4 K/min.

Before analysis, catalyst samples were thoroughly washed with pentane and dried in a vacuum of 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 [16].

Catalyst Formation and Hydrogenolysis of Alkanes and Cycloalkanes. We placed 0.127 g (0.5 mmole) OsO_4 and 50-100 mmoles saturated hydrocarbon into a 50 ml stainless steel autoclave and heated the solution at 150°C and P_{H_2} = 5 MPa for 3-15 h (see Table 1). Gaseous

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*EXAFS studies of the catalysts were performed by A. T. Shuvaev, B. Yu. Khel'mer, and F. M. Ovsyannikov.

products from the autoclave cooled to room temperature were condensed in a 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. For repeated use of the dry catalyst, freshly distilled hydrocarbon was placed into the autoclave, H_2 was added, and the mixture was heated at the selected temperature for 3-15 h. Cycles can be repeated by distilling 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 into an autoclave containing a thin-walled sealed glass ampul with a portion of OsO_4. H_2 was added. The ampul was broken and the contents of the autoclave were stored overnight and then heated at 180°C for 15 h. Product analysis and repeated use of the catalytic system was carried out as described for the previous experiment.

Catalyst Formation and Hydrogenation of Benzene and Toluene. A solution of 0.126 g (0.5 mmole) OsO_4 in 25-50 mmoles benzene or toluene was shaken in a steel autoclave at 20°C at P_{H_2} = 3 MPa for 3-4 days (induction period of one day), periodically adjusting the H_2 pressure to 3 MPa. After the pressure stopped falling, the cyclohexane and benzene (methylcyclohexane and toluene) were distilled from the autoclave and a new portion of benzene was added to the remaining catalyst under an Ar atmosphere. Heat was evolved and the hydrogenation occurred even more rapidly (at a mole ratio [ArH]:[Os] = 100:1, hydrogenation was completed with vigorous stirring after from 5 min to 3 h). Repetition of this cycle once or twice produced a catalyst capable of hydrogenating benzene at 20°C and 0.1 MPa H_2.

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!), cooling the autoclave from outside with a stream of air. After 1 h, the CPA formed was distilled from the autoclave. Yield, 90-98%.

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