Macromol. Symp. ***136****, 41-46 (1998)*

Cluster Carbonyls of Os, Fe and Fe-Rh on Oxide Supports: Synthesis and Properties

Boris N. Kuznetsov, Vladimir I. Kovalchuk, Nikolai V. Chesnokov,
Nadezhda M. Mikova, Lilia V. Naimushina

Institute of Chemistry and Chemical Technology Siberian Branch RAS
Akademgorodok, Krasnoyarsk, 660036, Russia

SUMMARY: Surface nano-size structures have been obtained by supporting on oxide supports (SiO_2, MgO, Al_2O_3) some cluster carbonyls of Os, Fe, Fe-Rh and by their following thermal conversions. Surface species were characterized by IR-spectroscopy, high-resolution TEM, XPS, Mössbauer spectroscopy and temperature-programmed desorption technique. Their catalytic properties was studied in CO hydrogenation reaction.

Introduction

The advantages in preparation of homo- and heteropolynuclear carbonyls of transition metals open a new possibilities for synthesis of surface nano-structures by carbonyl cluster immobilization on solid supports.

Different methods were suggested for synthesis of carbonyl compounds immobilized on oxide support surfaces. Some of them include the adsorption or chemical interaction between metal carbonyl and surface functional groups (OH-groups, or specially prepared P,N,S,O containing groups), the reactions of thermal transformation of surface carbonyl compounds[1-2].

At present time the various methods were elaborated for the synthesis of carbonyl compounds with different number and nature of metal atoms in cluster framework.

Some data concerning the use of carbonyl clusters of Os, Fe, Fe-Rh for synthesis of nano-size structures on surface of oxide supports (SiO_2, MgO, Al_2O_3) are presented and discussed in this paper.

CCC 1022-1360/98/$ 17.50

Cluster carbonyl synthesis

Conventional and original methods were used for synthesis of Fe, Os, Fe-Rh cluster carbonyls. Reactions of thermal transformation in diglyme were used for preparation of iron carbidocarbonyl clusters[3)] :

$$Fe(CO)_5 \xrightarrow[130\text{-}140^0C,\ 2h]{[Fe(CO)_4]^{2-}} [Fe_6C(CO)_{16}]^{2-} \xrightarrow[5\text{-}6\ h]{140\text{-}150^0\ C} [Fe_5C(CO)_{14}]^{2-} \qquad (1)$$

Clusters $[TEA][Fe_5RhC(CO)_{16}]$ ($TEA\text{-}(C_2H_5)_4N$) was prepared with high yield by addition to $[TEA]_2[Fe_5C(CO)_{14}]$ carbonyl $[Rh(CO)_2Cl]_2$ or hydrated Rh chlorides[4)].

Thermal transformation of this cluster in diglyme leads to pentanuclear cluster anions[4)]:

$$[TEA][Fe_5RhC(CO)_{16}] \xrightarrow[2h]{80\text{-}100^0\ C} [TEA]\ [Fe_4RhC(CO)_{14}], \qquad (2)$$

Various iron-containing Fe-Rh heteroatomic carbonyls were synthesized according to the scheme[5)]:

$$[TEA][Fe_4RhC(CO)_{14}] \begin{cases} \xrightarrow[25^0C,\ CH_2Cl_2]{[Rh(CO)_2Cl]_2} Fe_4Rh_2C(CO)_{16} \\ \\ \xrightarrow[70^0C,\ diglyme]{RhCl_3} [TEA][Fe_3Rh_3C(CO)_{15}] \end{cases} \qquad (3)$$

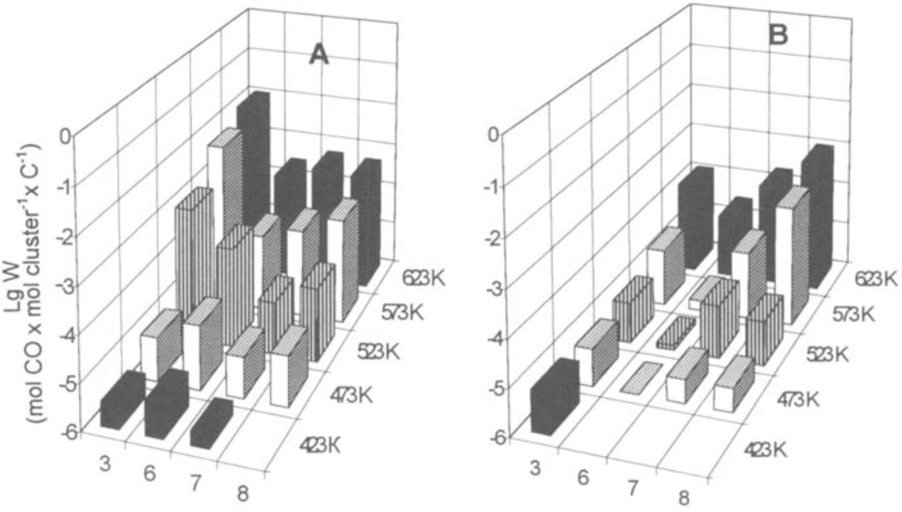
Osmium clusters $Os_3(CO)_{12}$[6)], $HOs_3(CO)_{10}OH$[6)], $Os_6(CO)_{18}$[7)], $Os_7(CO)_{21}$[7)], $Os_8(CO)_{24}$[7)] and iron carbonyls $[TEA][HFe(CO)_4]$[8)], $Fe_2(CO)_9$[9)], $[TEA]_2[Fe_2(CO)_8]$[8)], $Fe_3(CO)_{12}$[10)], $[TEA]\text{-}[HFe_3(CO)_{11}]$[10)], $[TEA]_2[Fe_4(CO)_{13}]$[11)], $Fe_5C(CO)_{15}$[12)] were obtained by known methods.

Supported carbonyls properties

According to IR-spectroscopy data the carbonyl cluster $HOs_3(CO)_{10}OH$ chemically interacts with OH-group of silica surface at room temperature, in contrast to complexes $Os(CO)_{12}$, $Os_6(CO)_{18}$, $Os_7(CO)_{21}$, and $Os_8(CO)_{24}$, which are only adsorbed by SiO_2 surface. All SiO_2-supported carbonyl clusters keep their initial nuclearity up to 523-573 K, and the highest thermal stability was observed for $HOs_3(CO)_{10}OH$. TEM data indicate that the size of Os surface species on SiO_2 ranges between 0.5-1 nm depending on the temperature. Supported on

MgO osmium carbonyls dissociate even at room temperature. At high temperature (≥ 623 K) metal species with size 0.5-2 nm were produced on MgO surface.

Supported on oxide surface Os carbonyl compounds demonstrate the activity in CO hydrogenation reaction and promote C_1-C_3-hydrocarbons formation. The comparison of catalytic activities of supported osmium clusters shows that Os/SiO_2-systems are much more active then Os/MgO samples (Fig. 1.).



The number of metal atoms

Fig. 1. Data on catalytic activity in CO hydrogenation reaction on SiO_2 (A) and MgO (B) supported osmium clusters with different nuclearity

It was shown that the labile and thermally unstable clusters (e.g. $Os_3(CO)_{12}$) have higher catalytic activity in comparison with the more stable supported clusters $HOs_3(CO)_{10}OH$ and $HOs_3(CO)_9(OH)PPh_3$.

Supported on SiO_2 iron carbonyls $[TEA][HFe(CO)_4]$, $Fe_2(CO)_9$, $[TEA]_2[Fe_2(CO)_8]$, $Fe_3(CO)_{12}$, $[TEA][HFe_3(CO)_{11}]$, $[TEA]_2[Fe_4(CO)_{13}]$, $Fe_5C(CO)_{15}$, $[TEA]_2[Fe_5C(CO)_{14}]$, $[TEA]_2[Fe_6C(CO)_{16}]$ have different reaction ability and thermal stability. According to temperature-programmed desorbtion (TPD) data silica-supported carbonyls with low nuclearity (Fe_1-Fe_3)

carbidocarbonyl clusters Fe_5-Fe_6 are more stable at this temperature range. Apparently interstitial carbon atom increases the thermal stability of silica supported $Fe_5C(CO)_{15}$, $[TEA]_2[Fe_5C(CO)_{14}]$, $[TEA]_2[Fe_6C(CO)_{16}]$ carbidocarbonyl clusters. According to TEM data the diameter of metal particles in reduced by H_2 at 623 K sample $[TEA]_2[Fe_6C(CO)_{16}]/SiO_2$ corresponds to the size of metallic frame of initial iron cluster (about 0.5 nm).

Supported iron carbonyls yield mainly the C_1-C_4 hydrocarbons. For majority of them the formation of different individual products in narrow temperature region was observed. The significant increase of specific catalytic activity (refered to per mole of supported cluster) with the variation of number of metal atoms in iron carbonyls from 1 up to 6 was detected. Most essentially this effect was manifested at relatively low reaction temperatures, in particular at 373 K (Tab.1.)

Tab.1. Data on catalytic properties in reaction of hydrocarbons synthesis from CO and H_2 on SiO_2-supported iron carbonyls of different nuclearity (pressure 0.1 MPa)

Catalyst	Temperature, K	Total activity$^{a)}$	Selectivity, wt.%			
			CH_4	C_2H_4	C_2H_6	C_3H_6
$[HFe(CO)_4]^-/SiO_2$	373	$1.69 \cdot 10^{-6}$	>99	-	-	-
	423	$1.57 \cdot 10^{-5}$	12	88	-	-
$[Fe_2(CO)_8]^{2-}/SiO_2$	423	$2.78 \cdot 10^{-6}$		3	97	-
	473	$1.30 \cdot 10^{-5}$	>99	-	-	-
$Fe_3(CO)_{12}/SiO_2$	373	$1.04 \cdot 10^{-5}$	<1	-	-	99.5
	423	$1.06 \cdot 10^{-5}$	<1	-	-	99.5
	473	$4.59 \cdot 10^{-5}$	9	32	-	59
$[HFe_3(CO)_{11}]^-/SiO_2$	373	$2.32 \cdot 10^{-6}$	76	24	-	-
	423	$1.19 \cdot 10^{-6}$	>99	-	-	-
	473	$7.5 \cdot 10^{-6}$	64	29	-	7
$[Fe_4(CO)_{13}]^{2-}/SiO_2$	373	$2.18 \cdot 10^{-5}$	28	72	-	-
	423	$2.66 \cdot 10^{-5}$	1	99	-	-
	473	$5.24 \cdot 10^{-4}$	-	99	1	-
	523	$9.32 \cdot 10^{-4}$	-	73	27	-
$Fe_5C(CO)_{15}/SiO_2$	373	$5.55 \cdot 10^{-5}$	2	-	-	98
	423	$2.4 \cdot 10^{-5}$	<1	2	-	98
	473	$6.21 \cdot 10^{-5}$	-	35	-	65
$[Fe_5C(CO)_{14}]^{2-}/SiO_2$	373	$1.27 \cdot 10^{-6}$	-	99	-	1
	423	$5.15 \cdot 10^{-4}$	1	99	-	-
	473$^{b)}$	$1.02 \cdot 10^{-3}$	23	58	12	4
$[Fe_6C(CO)_{16}]^{2-}/SiO_2$	373	$1.67 \cdot 10^{-4}$	31	49	20	-
	423	$2.93 \cdot 10^{-4}$	-	>99	-	-
	473	$6.36 \cdot 10^{-4}$	11	80	9	-

$^{a)}$mol CO (mol cluster)$^{-1}$ c^{-1}

$^{b)}$yield of C_4H_8 up 3 wt.%

Thermal behavior of supported on SiO_2, Al_2O_3 and MgO FeRh carbonyl clusters with different composition was studied. It was found that chemical transformations of supported FeRh clusters are similar to their chemical reactions in solutions. Already at 323 K the transformation of silica supported $[TEA][Fe_5RhC(CO)_{16}]$ to cluster $[TEA][Fe_4RhC(CO)_{14}]$ was observed. The latter yields the mixture of $[TEA][Fe_4Rh_2C(CO)_{16}]$ and $[TEA][Fe_3Rh_3C(CO)_{15}]$ after heating at 373-423 K :

$$[Fe_5RhC(CO)_{16}]^- + \equiv SiOH \xrightarrow{<100^0C} [Fe_4RhC(CO)_{14}]^- + (\equiv Si\text{-}O)_2Fe^{2+} + CO + H_2$$

$$[Fe_4RhC(CO)_{14}]^- + \equiv SiOH \xrightarrow{\approx 150^0C} Fe_4Rh_2C(CO)_{16} + [Fe_3Rh_3C(CO)_{15}]^- +$$
$$+ (\equiv Si\text{-}O)_2Fe^{2+} + CO + H_2 \qquad (4)$$

Supported on MgO $[TEA][Fe_5RhC(CO)_{16}]$ can be converted to mono- and dianions $[Fe_4RhC(CO)_{14}]^-$ and $[Fe_4Rh_2C(CO)_{15}]^{2-}$. In previous paper[13)] was reported that according to Mössbauer and TEM data the SiO_2-supported FeRh carbonyls produce bimetallic species with the size 0.5 nm after heating in the range 523-623 K. Results of XPS investigation of the these samples indicate the presence of iron mainly in the ionic forms (Fe^{2+},Fe^{3+}) and rhodium in the metallic form.

It was shown that supported FeRh clusters promote mainly the formation of ethanol and methanol in CO hydrogenation reaction at 523-573 K and 5 MPa.

Conclusion

It has been shown that by supporting of Os, Fe and FeRh carbonyl clusters on surface of SiO_2, Al_2O_3, MgO and by thermal conversion in different gaseous medium of supported carbonyl clusters the metal species can be obtained with size 05.-2 nm. The obtained nano-size surface structures have unique catalytic properties in CO hydrogenation reaction.

References

1) Yu.I. Yermakov, B.N. Kuznetsov, V.A. Zakharov, *Catalysis by supported complexes*, Elsevier, Amsterdam e.a. (1981)

2) B.C. Gates,L. Guczi, H. Knözinger, Eds. *Metal Cluster in Catalysis*, Elsevier: Amsterdam, (1986)

3) V.E. Lopatin, N.M. Mikova, S.P. Gubin, *Izv. Akad. Nauk, Ser. Khim.* **8**, 1925 (1981)

4) V.E. Lopatin, M.Ts. Tsybenov, N.M. Mikova, S.P. Gubin, *Koord. Khim.* **11**, 1099 (1985)

5) S.P. Gubin, N.M. Mikova, M.Ts. Tsybenov, V.E. Lopatin, *Koord. Khim.* **10**, 625 (1984)

6) C.R. Eady, B.F.G. Johnson, J. Lewis, *JCS, Dalt. Trans.* **23**, 2606 (1975)

7) B.F.G Johnson, J Lewis, *Phil. Trans. R. Soc. Lond. A.* **308**, 5 (1982)

8) J.R Case, M.C.J. Whitiner, *J. Amer Chem Soc.* **80**, 4632 (1960)

9) E.H. Braye, W. Hubel, *Inorg. Synth.* **8**, 178 (1966)

10) W. Hiber, Brendel, *Z.Anorg. Chem.* **289**, 324 (1957)

11) W. Hieber, R. Werner, *Chem. Ber.* **90**, 286 (1957)

12) R.P. Stewart, U. Anders and W.A.G. Graham, *J. Organom. Chem.* **32**, C49 (1971)

13) I. Kovalchuk, N.M. Mikova, N.V. Chesnokov, I.V. Naimushina, B.N. Kuznetsov, *J. Mol. Catal. A: Chem.* **107**, 329 (1996)