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Combined XPS and AFM Study of Cluster-Containing Polymers Based on Rh

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Summary: Rh_6- monomer and polymer-immobilized complexes have been characterized using XPS and AFM. Polymer-immobilized clusters were obtained by the reaction of $Rh_6(CO)_{15}CH_3CN$ with copolymer of allyldiphenylphosphine and styrene. AFM study shows the change of surface morphology of the above copolymers. XPS data demonstrated the change of charge state of Rh atoms under monosubstitution of the CO-group for Rh_6- monomer complexes as well as in copolymer cluster complexe after the catalysis process of hydrogenation.

Keywords: AFM; catalysts; metal-polymer complexes; XPS

Introduction

Cluster-containing polymers are of great interest as catalysts for different reactions, combining the advantages both of homogeneous catalysts and heterogeneous ones.[1] They may be obtained in two ways: by immobilization of cluster compounds on macroligands, or by polymerization reactions of some hypothetic monomers.[2-3] Heterogenization of metal clusters allows to isolate the intermediate products and to study the mechanism of catalytic reactions. This paper present the study of polymer-immobilized clusters and their catalytic properties using XPS and AFM.

Experimental

Polymer-immobilized clusters were obtained through polymer-analogous transformations in two stages: 1) the photolysis of an initial cluster (UV-radiation, $\lambda = 300$ nm) in the presence of an intermediate labile ligand of $Rh_6(CO)_{16} + CH_3CN \rightarrow Rh_6(CO)_{15}CH_3CN + CO$; 2) the reaction of $Rh_6(CO)_{15}CH_3CN$ with a copolymer of allyldiphenylphosphine and styrene. The catalytic properties of the cluster-containing copolymer were studied in hydrogenation of

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cyclohexene. Rh_6-cluster-containing polymers and their monomer complexes were characterized using X-ray photoelectron spectroscopy (XPS) and atom-force microscopy (AFM). XP-spectra were recorded on an ES-2401 electron spectrometer employing MgK_α exciting radiation (1253.6 eV) under the pressure of about 10^{-6} Pa. The instrument was calibrated such that $Au4f_{7/2}$ = 84.0 eV. The binding energies were referenced to the C1s peak from the hydrocarbon at 285.0 eV. The line location precision made up 0.2 eV. The P4-Solver and P47-Solver devices from NT-MTD company were used for the AFM investigation. Cantilever of the same company (250 μm long, 35 μm wide, and 1.1 μm thick) with the silicon tip curvature radius of ~10 nm were used.

Synthesis of Cluster-containing Polymers

Polymer-immobilized clusters were obtained via polymer-analogous reactions between Rh_6-clusters and macromolecular compounds. The copolymers of styrene and 4-vinylpyridine ($\bar{M}_n$ = 150,000-200,000) or allyldiphenylphosphine ($\bar{M}_n$ = 9,000-80,000) were used as initial macroligands (Table 1).

Table 1. The molecular-weights characteristics of the copolymers of styrene with 4-vinylpyridine (4-Vpy).

Sample	The ratio of 4-VPy:styrene, mol.%		$\bar{M}_n$	M_w	M_w/M_n
	monomeric mixture	copolymer			
1	62:38	60:40	208000	349000	1.68
2	35:75	30:70	148000	261000	1.76
3	18:82	22:78	168000	327000	1.95
4	4:95	8:92	150000	286000	1.91

They were synthesized by radical copolymerization in the bulk and in the presence of the radical initiator of azobisisobutyronitrile. The macrocomplexes containing 1.8 to 4.1 wt.% of Rh were obtained by the interaction of $Rh_6(CO)_{15}CH_3CN$ and copolymer of styrene with allyldiphenylphosphine in benzene. The macrocomplexes were isolated by precipitation using methanol. They were light-yellow powders. The molecular-weights of the macrocomplexes were lower than that for the initial copolymers (M_n = 56000, M_w = 140000, M_w/M_n = 2.50 and

M_n = 80000, M_w=169000, M_w/M_n= 2.11 for the macrocomplex and metal-free copolymer of styrene with allyldiphenylphosphine, respectively). By analogous procedures the macrocomplexes on the base of copolymers of styrene with 4-vinylpyridine were obtained. The contents of Rh were in the range of 3.1 to 12.7 wt.%.

The Characterization and Properties of Cluster-containing Polymers

The XPS-investigations have demonstrated the presence of two peaks at 308.9 eV and 309.9 eV in the Rh3$d_{5/2}$-spectrum of the initial complex $Rh_6(CO)_{16}$ (Fig.1).

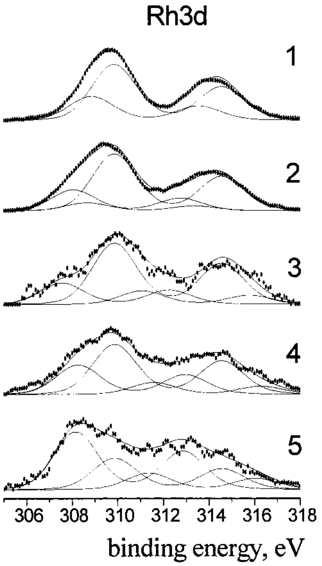
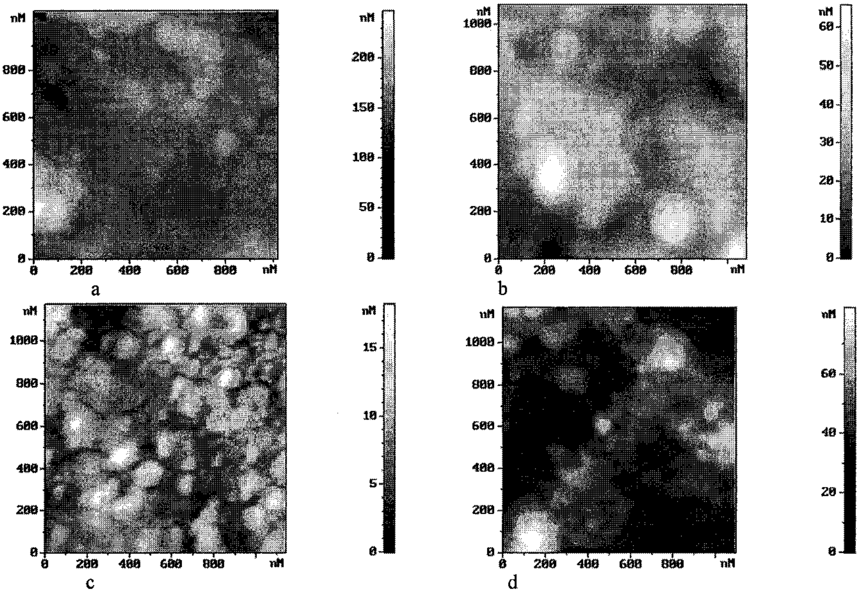


Fig. 1. XPS spectra Rh3d: 1 - $Rh_6(CO)_{16}$, 2 2- $Rh_6(CO)_{15}CH_3CN$, 3, 4, 5 – polymer immobilized clusters: 3–initial, 4, 5-after the first and the second hydrogenation, respectively.

The peak at 309.9 eV can be ascribed to the Rh atom in $Rh_6(CO)_{16}$. The chemical structure of complex influenced the binding energy of Rh3$d_{5/2}$ electrons For Rh atoms in $Rh(CO)_2Cl$ E_b Rh3$d_{5/2}$ = 309.2 eV [3], and in $Rh(CO)_2$ - E_b Rh3$d_{5/2}$ = 309.1 eV. [4] The line at 308.9 eV (Fig.1, curve 1) may have resulted from the cluster decarbonylation in vacuum under X-ray radiation. A similar shift (0.9 eV) to lower binding energies was observed under the loss of a CO-group in $Rh(CO)_2$.[5] The monosubstitution of a CO-group by the CH_3CN ligand results in a new line at 308.2 eV (Fig.1, curve 2). The line shift to the binding energies lower than those of the initial complex is quite justified, because the CO-group is replaced by a less electronegative group. The decrease of the line intensity at 308.9 eV (Fig.1, curve 2) implies a lower decarbonylation of this sample in comparison with the initial one. The interaction of the cluster with copolymer of allyldiphenylphosphine and styrene results in a line shift from the binding energy of 308.2 eV to 307.1 eV (Fig. 1, curve 3), witnessing a partial reduction of Rh atoms. When cyclohexene is hydrogenated in the presence of a copolymer, some oxidation of Rh atoms takes place. This results in the low energy peak shift to 308.3 eV (Fig.1, curve 4), and the appearance of a new line at 311,5 eV. Besides, hydrogenation is accompanied by the intensity decrease of the main peak in the Rh3$d_{5/2}$-spectrum and hence, by the growth of a low-energy peak at spectrum. The line intensity ratio of the initial copolymer is equal to 1:3.3, with the 1:1.8 after the first hydrogenation and 1:0.5 after the second one.

The samples for AFM study were prepared by the dissolution of the copolymer powder in toluene with the following drying. The AFM-investigation of the topography of the pure copolymer shows that it represents the 70-100 nm spherical particles distributed rather uniformly along the substrate (Fig. 2a). The AFM-investigation of the topography of the cluster copolymer samples demonstrated that the obtained samples represent particles with a shape close to spherical (Fig. 2b), distributed rather uniformly along the substrate. It is seen that the 50-100 nm particles dominated, which in their turn united into large aggregates (Fig. 2b). At the same time a 20 nm particles are observed.

After hydrogenation the aggregation capability becomes lower and the tendency for decrease of particles size takes place (Fig. 2c,d).



a b c d

Fig. 2. AFM- topography of samples: a - the pure copolymer of allyldiphenylphosphine and styrene, b,c,d - the cluster copolymer; b initial, c - after the first hydrogenation, d - after the second hydrogenation.

The polymer immobilized clusters obtained is catalytically fairly active. Although during the first cycle of hydrogenation of cyclohexene its speed was not high (0.015 mole/(g-atom Rh s)), with a larger number of cycles, the reaction speed increased and reached 2 moles /(g-atom Rh s). The kinetic curves of hydrogen absorption during the cyclohexene hydrogenation in the presence of the immobilized copolymer demonstrated the presence of an induction period in the first cycle and the increase of catalyst activity when used in the following cycles (Fig. 3).

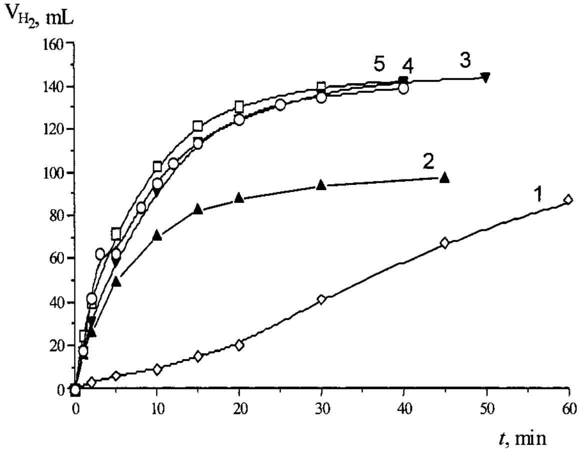


Fig. 3. The consumption of H_2 in the hydrogenation of cyclohexene in the presence of $Rh_6(CO)_{15}CH_3CN$ polymer-immobilized catalyst (T = 40°C, isopropyl alcohol, the curve numbers indicate the cycle numbers, [cyclohexene] 1,2 – 4, 5 mmole, 3,4,5 – 6, 5 mmole).

This enables a multiple use of the catalyst. The results obtained allows an assumption to be made of a cluster fragmentation during hydrogenation, followed by the formation of low concentrations of highly active particles with lower nucleation (possibly – mononuclear), which are true catalysts. The fact that no coordination vacancies are present in the carbonyl clusters of Rh_6, its cluster-containing monomers and polymers included, also speaks in favor of such an assumption.

The cluster heterogenization enabled the isolation of the catalyst from the reaction medium, as well as its multiple use in new catalytic cycles. Probably, coordination vacancies form as a result of Rh-Rh bond ruptures in the Rh_6-cluster. This promotes the hydrogen molecule activation and the formation of hydride cluster species with lower (and, possibly, larger) nucleation, to which the XPS and AFM-data is indirect evidence.

Conclusion

The Rh-based cluster-containing polymers obtained through polymer-analogous transformations, manifest high catalytic activity in hydrogenation reactions. They can be removed from a reaction medium and be repeatedly used, being active in the following cycles. It is most probable, that during the hydrogenation reaction the cluster fragmentation occurs with the formation of active species that include cluster structures of lower nucleation, and, may be, mononuclear complexes stabilized with the polymer matrix.

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