ICEM2010-($% *

MACROPOROUS CATALYSTS FOR HYDROTHERMAL OXIDATION OF METALLORGANIC COMPLEXES AT LIQUID RADIOACTIVE WASTE TREATMENT

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ABSTRACT

One of the main problems of liquid radioactive waste (LRW) management is concerned with treatment of decontamination waters containing organic ligands. The organic ligands like oxalic, citric and ethylenediaminetetraacetic acids form stable complexes with radionuclides which puts restrictions on application of many technologies of LRW management. One of the ways of destruction of metallorganic complexes consists in using the catalytic oxidation. However, the heterophase catalytic oxidation is rather problematic due to formation of metal oxides on the catalyst surface and calmatation of meso- and micropores. A possible solution of the above problem can be found in synthesis of macroporous catalysts for oxidation having a regular macroporous structure.

The present paper describes the template synthesis of macroporous metalloxide catalysts performed with using siloxane-acrylate microemulsions as templates. The method for impregnation of precious metals (PM) particles into the template, which enables one to produce PM nanoparticles of a specific size and immobilize them in the porous structure of the synthesized metalloxide catalysts, is presented. A possible mechanism of the synthesis of macroporous catalysts is suggested and the comparison of the electronic and photon-correlation spectroscopy results obtained at different stages of catalysts synthesis was conducted.

KEYWORDS: Radionuclide organic complexes oxidation; macroporous catalysts; template synthesis; siloxane-acrylate microemulsions; precious metals impregnation.

INTRODUCTION

Manganese oxides keep finding an extensive application as oxidation catalysts [1]. Recently, efficient manganese-oxide catalysts used for oxidation and containing nanoparticles of precious metals, in particular, gold, have been synthesized [2-3]. Studies of the manganese oxide porous structure are mainly concerned with micro- and mesopores formed in the process of the oxide synthesis [1]. At the same time, the macroporous structure of the synthesized oxides is virtually not controlled while it could have a substantial effect on the material catalytic and electrochemical properties. For example, it was established that use of catalysts in oxidation of metallo-organic complexes of transition metals was often accompanied by calmatation of the catalysts micropores with the formed metal oxides and hydroxides (see, for example, [4]) and, as result, a loss of the catalytic properties.

In some cases, obtaining a regular macroporous structure is possible through leaching glasses and ceramics with heterophase structures [5]. Another method to obtain the above structure is a template synthesis of materials using organic templates with sufficiently large particle sizes (polymer

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solutions and emulsions), which enable one to produce materials with essentially macroporous structures [6]. In the latter case, using the emulsions serving as components of the template synthesis as nanoreactors for producing precious metals nanoparticles [7, 8], one can substantially simplify the technique of the synthesis of catalysts having the precious metals in the ordered macroporous structure.

One should mention that producing macroporous manganese oxides with a pre-determined solid phase composition by means of the template synthesis methods comprises a rather complicated task due to the large set of processes resulting from phase transitions in oxides under respective temperatures and gas medium properties required to remove the template.

The objective of the present study was the development of new methods of the template synthesis of macroporous catalysts for liquid-phase and hydrothermal oxidation on the basis of manganese oxides containing gold nanoparticles using acrylate emulsions.

EXPERIMENTAL

The commercially available acrylate emulsion KE 13-36 (solid phase content 50%, average particle size 160 nm) produced by JSC "Astrokhim" (Elektrostal', Moscow Oblast) was used as a template. The colloid properties of the emulsion were described in [9, 10].

The synthesis of emulsion containing gold nanoparticles was performed through addition of the required amount of $H[AuCl_4]$ to the emulsion solution in 0.05N NaOH followed by the heating at 100°C during 30 minutes. In the above process the treated emulsion acquires a characteristic color ranging from pink (1 mg Au per 1 g of dry emulsion polymer) to grey-blue (more than 2.5 mg Au per 1 g of dry emulsion polymer) which results from light absorption by plasmon gold particles [11].

The synthesis of the macroporous material was performed in accordance with the following scheme. 50 ml of diluted emulsion (solid content 5%) was added with the manganese (II) chloride solution (0.95 g $MnCl_2 \cdot 4H_2O$ in 15 ml of water) containing 25 mg of chitosan chloride under constant mixing and, further, the solution containing 0.76 mg of potassium permanganate in 75 ml of water. The addition of chitosan is necessary to reduce the charge of emulsion particles and control the formation of the manganese (IV) oxide gel. After two-hour mixing the solution was filtered, rinsed with distilled water and dried at 90°C. The obtained material was then annealed in the atmosphere with the controlled oxygen content at 200-900°C to remove the organic template.

The specific surfaces of the produced meso- and macroporous materials were determined on the device "Sorbtometr-M" (Institute of Catalysis, Siberian Department, Russian Academy of Sciences, Novosibirsk, Russia). The pore size distribution was determined on mercury porosimeter "AutoPore IV" (Micromeritics Co., Ltd., USA). TEM and SEM

images were obtained with transmission electronic microscope Zeiss LIBRA 200FE (Germany) and scanning electronic microscope Hitachi S-550 (Japan), respectively.

The catalytic activity of the produced compounds in regard to the liquid-phase oxidation of the dyeing agent (methylene blue – MB) by hydrogen peroxide was determined on the flow-type catalytic installation with the reactor volume 5 ml.

Hydrothermal oxidation on macroporous catalysts was performed on the flow-type hydrothermal oxidation installation described in [12].

RESULTS AND DISCUSSION

The production of nanoparticles of precious metals by the thermal reduction in polymer solutions is a well-known process [11]. Here we used the thermal reduction of gold in the emulsion containing acrylate carboxyl groups. The particles of the reduced gold are implanted into the emulsion particles, as seen from the respective TEM image in Fig. 1, which comprises a general scheme of the macroporous manganese oxides synthesis.

After the addition of precursors of inorganic hydroxide (in this case – manganese (II) chloride and potassium permanganate) into the emulsion solution containing gold particles, the manganese (IV) hydroxide gel is formed. The solution separated during the filtration does not contain gold within the ICP-determination error range, i.e. more than 99.5% of gold is transferred into the solid phase. Nevertheless, there exists another possibility for the loss of gold nanoparticles during their impregnation into a macroporous material through the template synthesis with gold-containing emulsions – it is concerned with the stage of the organic template annealing. However, the comparison of the gold amount before and after the above stage confirms that the losses are insignificant and do not usually exceed 1-3%.

Substantial differences in both chemical and structural properties of porous manganese oxides obtained through the template synthesis are revealed under different conditions of the organic template annealing (see Fig. 1). Here the sample porous structure depends to a great extent on the oxygen content in the atmosphere during sample heating. At heating on air the material inflammation occurs between 150 and 350°C depending on the heating rate. The inflammation destroys the macroporous structure. On the other hand, reduction of the oxygen content in the atmosphere during annealing enables one to obtain materials with more regular porous structure.

Fig. 2 shows Hg intrusion curves of the samples obtained at template annealing on air, 21% of oxygen (curve 1) and in the atmosphere containing 2% of oxygen (curve 2). One can see that in the first case the mercury intrusion into the sample corresponds to virtually continuous pore size distribution from a few microns down to tens of nanometers, while in the second case a relatively narrow size distribution close to that of the KE 13-36 emulsion is observed.

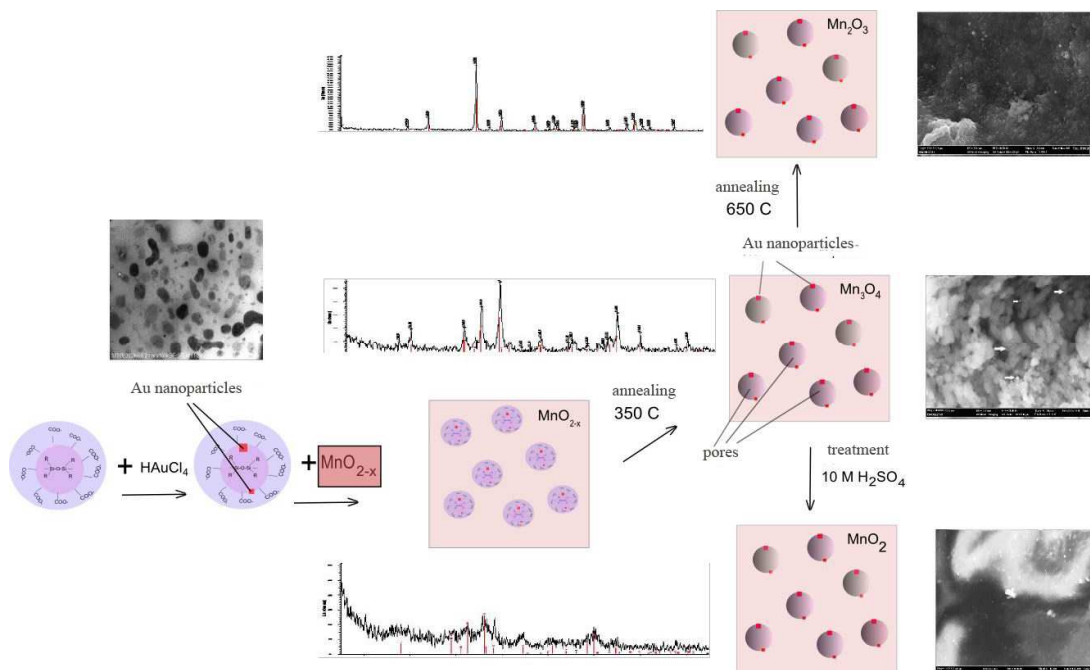2   Copyright © 2010 by ASME

Fig. 1. General setup of the macroporous manganese oxides synthesis.

By increasing the annealing temperature up to 650°C, it is possible to obtain the manganese (III) macroporous oxide with lower pore volume but with the same pore radius (Fig. 2, curve 3).
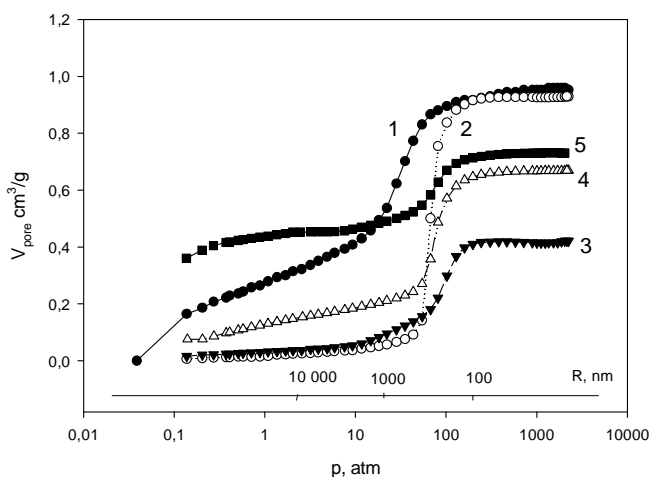

Fig. 2. Mercury intrusion curves of macroporous manganese oxides samples, containing 0.055 mass.% of gold, obtained with annealing at 350°C and O_2 content 21% (1); at 350°C and O_2 content 2% (2); two-stage annealing at 350°C and 650°C, O_2 content 21% (3); sample (2) after treatment with sulfuric acid (4); sample (2) after usage in hydrothermal reactor (5).

Table 1. Parameters of porous structure of macroporous manganese oxides samples.

Sample (annealing conditions)	Phase composition	S_{spec} m^2/g	V_{mac}, cm^3/g
M-1 (t=350°C, 2% O_2)	hausmannite	31.0	0.92
M-2 (t=350°C 2% O_2 + 650°C 21% O_2)	bixbyite+ hausmannite	19.6	0.38
M-4 (t=350°C 2% O_2 + 0.1 M H_2SO_4 150°C)	hausmannite+ gamma-MnO_2	176.1	0.65

Another way of producing the porous manganese dioxide in different crystalline forms consists in treatment of the manganese porous oxide hausmannite with sulfuric acid of some specific concentrations [13, 14]. In this case it becomes possible to substantially modify the nature of the porous structure and attain formation of meso- and micropores [13]. In our work we used the method consisting in impregnation of a porous hausmannite sample with 0.1M solution of sulfuric acid. In this method the amount of the 0.1M solution of sulfuric acid was selected to produce its 10M solution in the known macropore volume after drying at 150°C. Here if we take a limited amount of sulfuric acid, more homogeneous sample with high specific surface can be produced (Fig. 2 and Table 1).

Application of the above materials as oxygen catalysts was tested in the liquid-phase oxidation of a thiazine dye (methylene blue – MB) by hydrogen peroxide (HP) at 25°C. Fig. 3 shows the change of the optical density at λ=661 nm (MB maximum absorption) at different times of the presence

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of the HP-containing solution in the reactor filled with different macroporous manganese oxides. One can see that introduction of gold nanoparticles into the manganese oxide porous system results in significant increase of the rate of the MB liquid-phase oxidation by hydrogen peroxide. The macroporous manganese oxide obtained by treatment with sulfuric acid appears to be the most efficient catalyst of the liquid-phase oxidation.

One of the applications of the liquid-phase oxidation macroporous catalysts comprises the catalytic oxidation of metallorganic complexes of radionuclides under hydrothermal conditions being one of the stages of modern technologies of concentrated liquid radioactive waste (LRW) management [12, 15].

The advantages of high-temperature (hydrothermal and supercritical) methods of LRW decontamination from cobalt and other transition metals radionuclides results from the instability of organic complexes of the mentioned metals at high temperatures – the chemical equilibrium in solutions shifts to formation of transition metals oxides with simultaneous very fast oxidation and thermal destruction of organic ligands under hydrothermal and supercritical conditions [12].
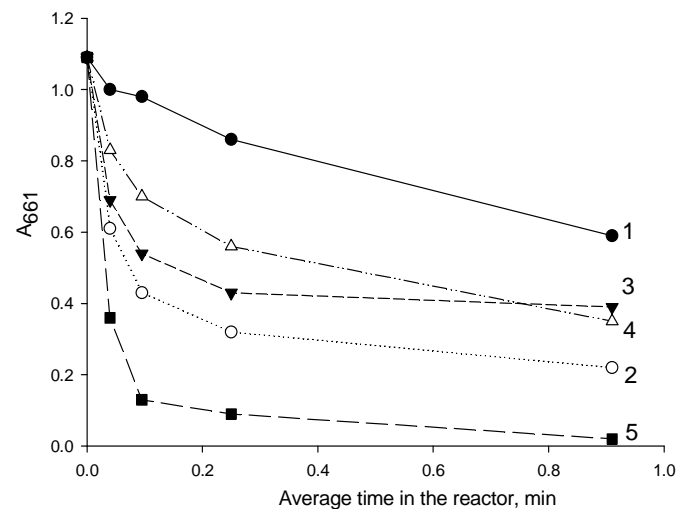

Fig. 3. Catalytic oxidation of methylene blue by hydrogen peroxide with application of macroporous manganese oxides obtained with annealing at 500°C (1); macroporous manganese oxides containing 0.055 mass. % of gold nanoparticles and annealed at 500°C (2), 350°C (3), 650°C (4); sample (2) treated with sulfuric acid (5). All samples were pre-annealed at 350°C and O_2 content 2%.

The occurring reactions can be written as:
at low temperature: $Me\ L^- + n\ O^* = R\text{-}O\text{-}\{Me\text{-}O\text{-}Me\}_x\text{-}OR$;
at high temperature: $Me\ L^- + n\ O^*\ (t) = MeO_2 + R\text{-}COO^-$,

where $Me\ L^-$ – radionuclide metallorganic complex; $R\text{-}O\text{-}\{Me\text{-}O\text{-}Me\}_x\text{-}OR$ – polynuclear metalloxide complex stabilized by oxidized complex of the ligand L ($R\text{-}COO^-$); MeO_2 – metal (radionuclide) oxide. Oxidation of transition metals organic complexes at high temperature is catalyzed by transition metals oxides.

The macroporous character of the catalysts for hydrothermal oxidation of metallorganic complexes is crucial to prevent calmatation of a porous system by transition metals oxides formed at hydrothermal oxidation [12]. The latter can be provided by application of catalysts on the basis of manganese oxides containing gold nanoparticles. Fig. 4 shows the dependencies of the hydrothermal oxidation of the Co-EDTA complex for different catalysts produced by the template synthesis.

As was mentioned before, the hydrothermal approach to radionuclide-containing organic complexes destruction consists in creating conditions (in this case high temperature and high pressure) which would make these complexes highly unstable. On the other hand, industrial-scale application of such a technology at nuclear power plants (NPP) is concerned with high energy consumption. That is why attainment of the highest values of the oxidation temperature reduction is crucial in improvement of the respective technology efficiency. Fig. 4 demonstrates that during the process of the temperature increase a substantial reduction of Co-EDTA complexes concentration at oxidation using plain macroporous Fe and Mn oxides as catalysts or without any catalyst can be observed at about 170ºC (the lowest value), while the application of precious metals nanoparticles (gold) enables one to reduce the above temperature by approximately 20ºC. In other words, it is evident that the macroporous manganese oxides containing gold nanoparticles produce the largest value of the hydrothermal oxidation temperature reduction and, therefore, make it possible to significantly improve the process efficiency in terms of power consumption.

The insert in Fig. 4 presents the Co decontamination factors at prolonged treatment of solutions of cobalt and copper complexes with EDTA in hydrothermal reactor in the presence of macroporous catalysts. One can see that, in spite of the substantial amount of the formed precipitate of cobalt and copper oxides (about 1 g or 0.18 cm^3 per 1 g of the catalyst), the hydrothermal decontamination factor is preserved on a very high level. One should mention that transition metals hydroxides precipitates modify the macroporous catalyst porous structure (Fig. 2, curve 5) due to formation of crystal oxides of cobalt and copper, while the catalyst active centers, probably, do not undergo calmatation, which is the reason of a long-term catalyst performance. The latter is one of the most important parameters of the process efficiency, since the hydrothermal reactor does not undergo regeneration, but, after the process completion, it is sealed and further treated as a solid radioactive waste (SRW).

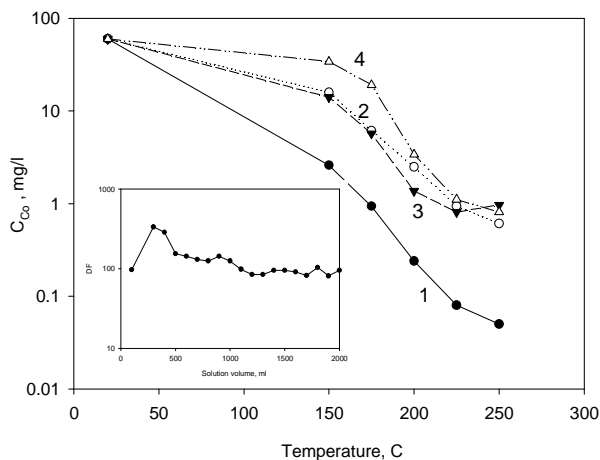4   Copyright © 2010 by ASME

Fig. 4. Hydrothermal oxidation of Co-EDTA complex in the solution Co-Cu-EDTA on macroporous manganese oxides containing 0.055 mass % of gold (1); without gold (2); on macroporous Fe(III) oxides (3); without catalyst (4). Insert: the change of the solution Co decontamination factor (DF) with the changing volume of the treated solution at 175°C using catalyst (1).

ACKNOWLEDGMENTS

REFERENCES

[1] Brock, S.L., Duan, N., Tian, Z.R., Giraldo, O., Zhou, H., and Suib, S.L., 1998, "A Review of Porous Manganese Oxide Materials," Chem. Mater., 10(10), pp. 2619-2628.

[2] Chang, L-H., Sasirekha, N., Rajesh, B., and Chen, Y-W., 2007, "CO Oxidation on Ceria- and Manganese Oxide-Supported Gold Catalysts," Separ. Purif. Technol., 58(1), pp. 211-218.

[3] Wang, L.-C., Liu, Q., Huang, X.-S., Liu, Y.-M., Cao, Y., and Fan, K.-N., 2009, "Gold Nanoparticles Supported on Manganese Oxides for Low-Temperature CO Oxidation," Appl. Catal. B: Environmental, 88(1-2), pp. 204-212.

[4] Gabelica, Z., Charmot, A., Vataj, R., Soulimane, R., Barrault, J., and Valange, S., 2009, "Thermal Degradation of Iron Chelate Complexes Adsorbed on Mesoporous Silica and Alumina," J. Therm. Anal. Calorim., 95(2), pp. 445-454.

[5] Toberer, E.S., and Seshadri, R., 2005, "Spontaneous Formation of Macroporous Monoliths of Mesoporous Manganese Oxide Crystals," Adv. Mater., 17(18), pp. 2244-2246.

[6] Imhof, A., and Pine, D.J., 1997, "Ordered Macroporous Materials by Emulsion Templating," Nature, 389(6654), pp. 948-951.

[7] Seregina, M.V., Bronstein, L.M., Platonova, O.A., Chernyshov, D.M., Valetsky, P.M., Hartmann, J., Wenz, E., and Antonietti, M., 1997, "Preparation of Noble-Metal Colloids in Block Copolymer Micelles and Their Catalytic Properties in Hydrogenation," Chem. Mater., 9(4), pp. 923-931.

[8] Bronstein, L., Kramer, E., Berton, B., Burger, C., Forster, S., and Antonietti, M., 1999, "Successive Use of Amphiphilic Block Copolymers as Nanoreactors and Templates: Preparation of Porous Silica with Metal Nanoparticles," Chem. Mater., 11(6), pp. 1402-1405.

[9] Avramenko, V.A., Bratskaya, S.Yu., Egorin, A.M., Tsarev, S.A., and Sergienko, V.I., 2008, "Colloid-Stable Nanosized Selective Sorbents for Decontamination of Bulk Materials," Doklady Chemistry, 422(2), pp. 251-254.

[10] Avramenko, V.A., Bratskaya, S.Yu., Egorin, A.M., Markovtzeva, T.G., Ryabushkin, A.N., and Harjula, R., 2008, "Nanosize Latexes Containing Polyacrylic Acid and Their Role in Transfer and Fixation of Radionuclides at Nuclear Energy Facilities," Russ J. Rad. Safety, (4), pp. 23-29 [in Russian].

[11] Koetz, J., and Kosmella, S., Polyelectrolytes and Nanoparticles, 2007, Springer, New York, NY, USA, 105 pp.

[12] Avramenko, V.A., Bratskaya, S.Yu., Voit, A.V., Dobrzhanskiy, V.G., Egorin, A.M., Zadorozhnyi, P.A., Mayorov, V.Yu., and Sergienko, V.I., 2009, "Application of Flow-Type Hydrothermal Method in Treatment of Concentrated Liquid Radioactive Waste of Nuclear Power Plants," Russ. J. Chem. Technol., 10(5), pp. 307-314 [in Russian].

[13] Sinha, A.K., Suzuki, K., Takahara, M., Azuma, H., Nonaka, T., Suzuki, N., and Takahashi, N., 2008, "Preparation and Characterization of Mesostructured gamma-Manganese Oxide and Its Application to VOCs Elimination," J. Phys. Chem. C, 112(41), pp. 16028-16035.

[14] Wang, F., Wang, Y.-M., Wen, Y.-X., Su, H.F., and Li, B., 2010, "Structural and Morphological Transformation of MnO_2 Nanostructures from Mn_3O_4 Precursor," Acta Phys.-Chim. Sin., 26(2), pp. 521-526.

[15] Worl, L.A., Buelow, S.J., Padilla, D.D., 2000, "Hydrothermal Processing," Challenges in Plutonium Science, N.G. Cooper, ed., Los Alamos Science, Los Alamos, NM, USA, p. 450.

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