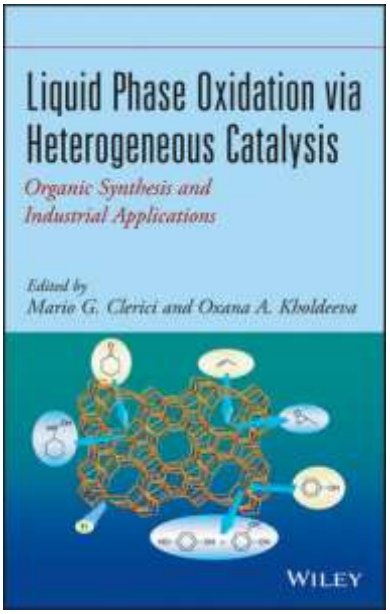
Main accomplishments

1. **Analysis of the state-of-the-art in the field of selective liquid-phase oxidation and use of heterogeneous catalysts for production of oxygen-containing products and intermediates of organic synthesis.**

Liquid Phase Oxidation via Heterogeneous Catalysis: Organic Synthesis and Industrial Applications, eds. M.G. Clerici and O.A. Kholdeeva, John Wiley & Sons, Inc., Hoboken, New Jersey, 2013, pp. 526.

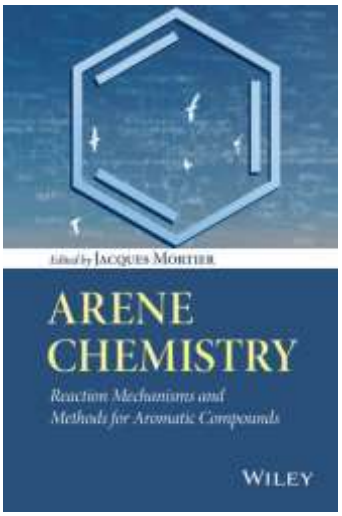


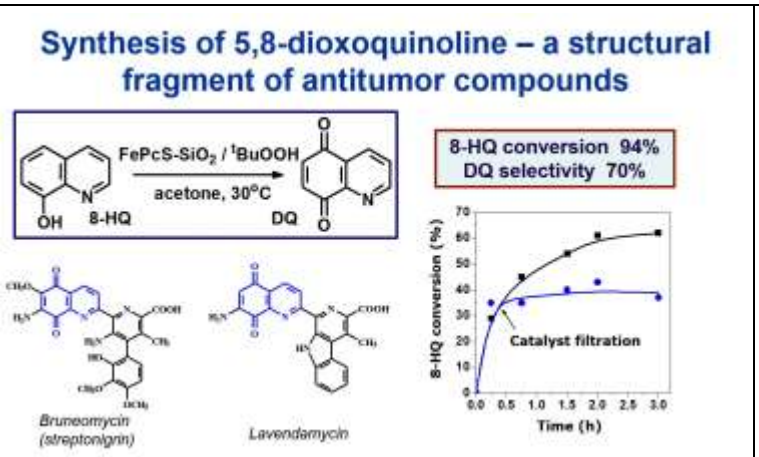
With the recent emphasis on green chemistry in the chemical industries, there is the need for environmentally friendly large-scale syntheses. This book lays out an important catalytic reaction class for these green/sustainable reactions, covering catalyst characterization and performance as well as paying special attention to catalyst stability and recyclability. An international team of authors guides readers in the selection, preparation, and use of catalysts for industrial organic synthesis in the pharmaceutical, fragrance, fine chemical, and petrochemical industries.

2. **Analysis of the state-of-the-art in the field of selective oxidation of aromatic rings with environmentally benign oxidants and development of new methods for production of substituted quinones.**

Review papers:

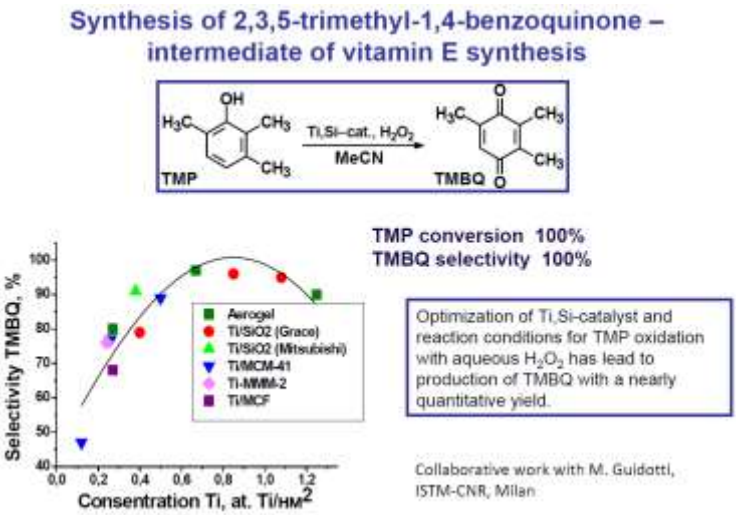
O. A. Kholdeeva, O. V. Zalomaeva, Recent advances in the transition-metal catalyzed selective oxidation of phenols and methoxyarenes using environmentally benign oxidants, *Coord. Chem. Rev.* 2016, 306, 302-330.

	O. A. Kholdeeva, Selective Oxidation of Aromatic Rings, In *Arene Chemistry: Reaction Mechanisms and Methods for Aromatic Compounds*, Ed. J. Mortier, Wiley, 2016, Ch. 14, p. 365-398.		O. A. Kholdeeva, Oxidation of phenols, in *Applied Homogeneous Catalysis with Organometallic Compounds*, Eds. B. Cornils, W. A. Hermann, M. Beller, R. Paciello, Wiley-VCH, 2017, p. 545-570.



O.V. Zalomaeva, O. A. Kholdeeva, A. B. Sorokin, Clean catalytic oxidation of 8-hydroxyquinoline to quinoline-5,8-dione with *t*-BuOOH in the presence of supported iron phthalocyanines, *Green Chemistry*, **2010**, 12, 1076 – 1082.

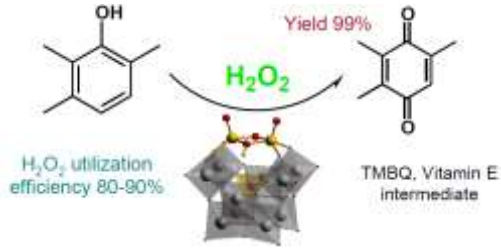
Collaborative work with Dr. A.B. Sorokin (IRC Lyon, France)



O. A. Kholdeeva, I. D. Ivanchikova, M. Guidotti, C. Pirovano, N. Ravasio, M. V. Barmatova, Y.A. Chesalov**,** Highly selective H_2O_2-based oxidation of alkylphenols to benzoquinones over silica-supported titanium catalysts: Ti cluster site *versus* Ti single site, *Adv. Synth. Catal*., **2009**, 351, 1877-1889.

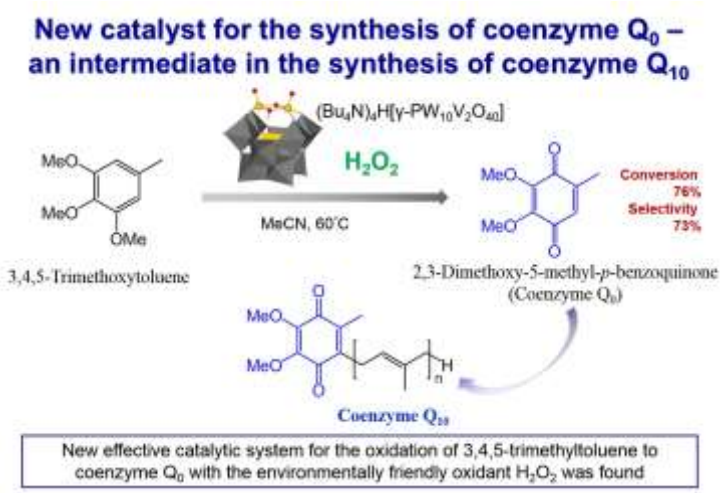
O.A. Kholdeeva, I.D. Ivanchikova, M. Guidotti, N. Ravasio, M. Sgobba, M. Barmatova, How to reach 100% selectivity in H_2O_2-based oxidation of 2,3,6-trimethylphenol to trimethyl-*p*-benzoquinone over Ti,Si-catalysts, *Catal. Today*, **2009**, 141, 330-336.

Europacat-8, Turku, 2007, *key-note lecture*



I. D. Ivanchikova, G. M. Maksimov, O. A. Kholdeeva, RU Patent 2568645, 20.11.2015.

I. D. Ivanchikova, N.V. Maksimchuk, R. I. Maksimovskaya, G. M. Maksimov, O. A. Kholdeeva, Highly selective oxidation of alkylated phenols to *p*-benzoquinones with aqueous hydrogen peroxide catalyzed by divanadium substituted polyoxotungstates. *ACS Catalysis*, **2014**, 4, 2706-2713.

	O. V. Zalomaeva, V.Yu. Evtushok, G.M. Maksimov, R.I. Maksimovskaya, O. A. Kholdeeva, Synthesis of coenzyme Qo through divanadium-catalyzed oxidation of 3,4,5-trimethoxytoluene with hydrogen peroxide, *Dalton Transactions*, **2017**, 46, 5202–5209. O. A. Kholdeeva, O. V. Zalomaeva, V.Yu. Evtushok, RU Patent 2628457, 17.08.2017.

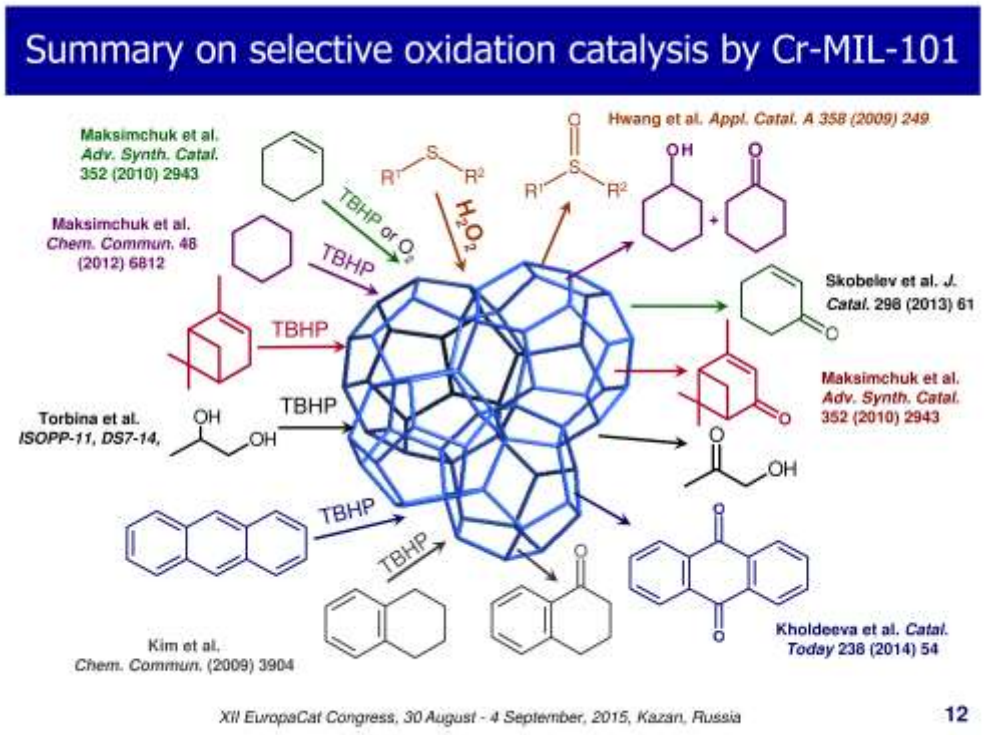
3. **Analysis of potential applications of metal-organic frameworks as heterogeneous catalysts in liquid-phase processes (selective oxidation, carboxylation).**

Review papers:

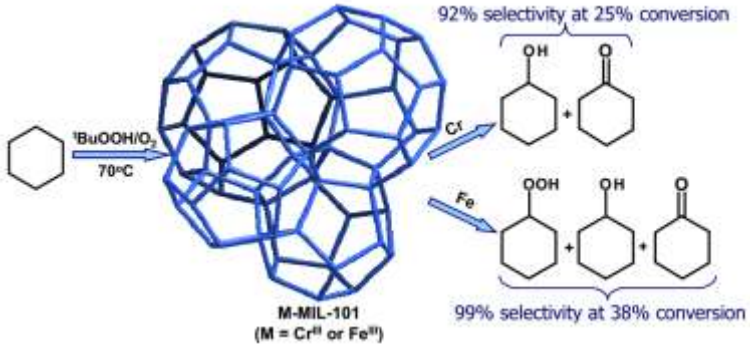
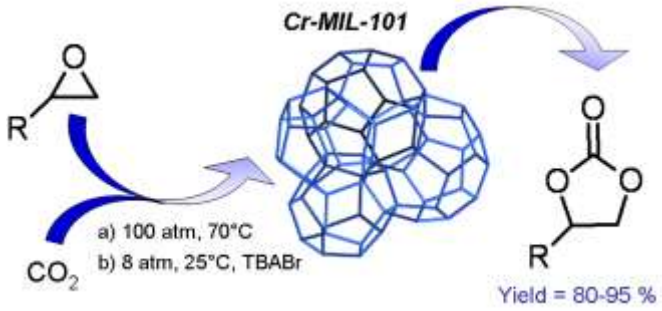
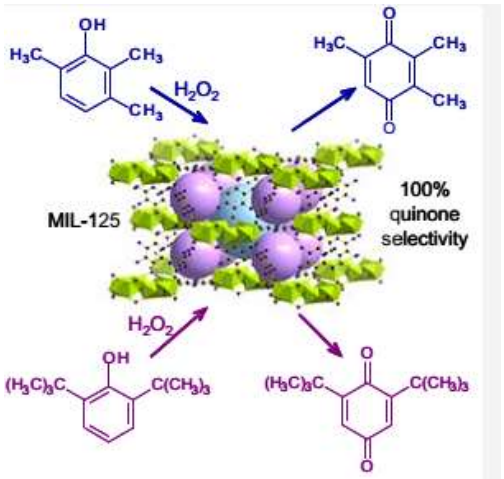
N. V. Maksimchuk, O. V. Zalomaeva, I. Y. Skobelev, K. A. Kovalenko, V. P. Fedin, O. A. Kholdeeva, Metal-organic frameworks of the MIL-101 family as heterogeneous single-site catalysts. *Special Issue "Recent Advances in Single-Site Heterogeneous Catalysis" (guest ed. J.M. Thomas), Proc. R. Soc. A*, **2012**, 468(2143) 2017-2034

O.A. Kholdeeva, Liquid-Phase Selective Oxidation Catalysis with Metal-Organic Frameworks, 12th European Congress on Catalysis – EuropaCat-XII, ISO meeting, Kazan, Russia, 30 August –4 September, 2015, Book of abstracts, p. 44 (*key-note lecture*);

O.A. Kholdeeva, Liquid-Phase Selective Oxidation Catalysis with Metal-Organic Frameworks, *Catal. Today*, **2016,** 278, 22–29.

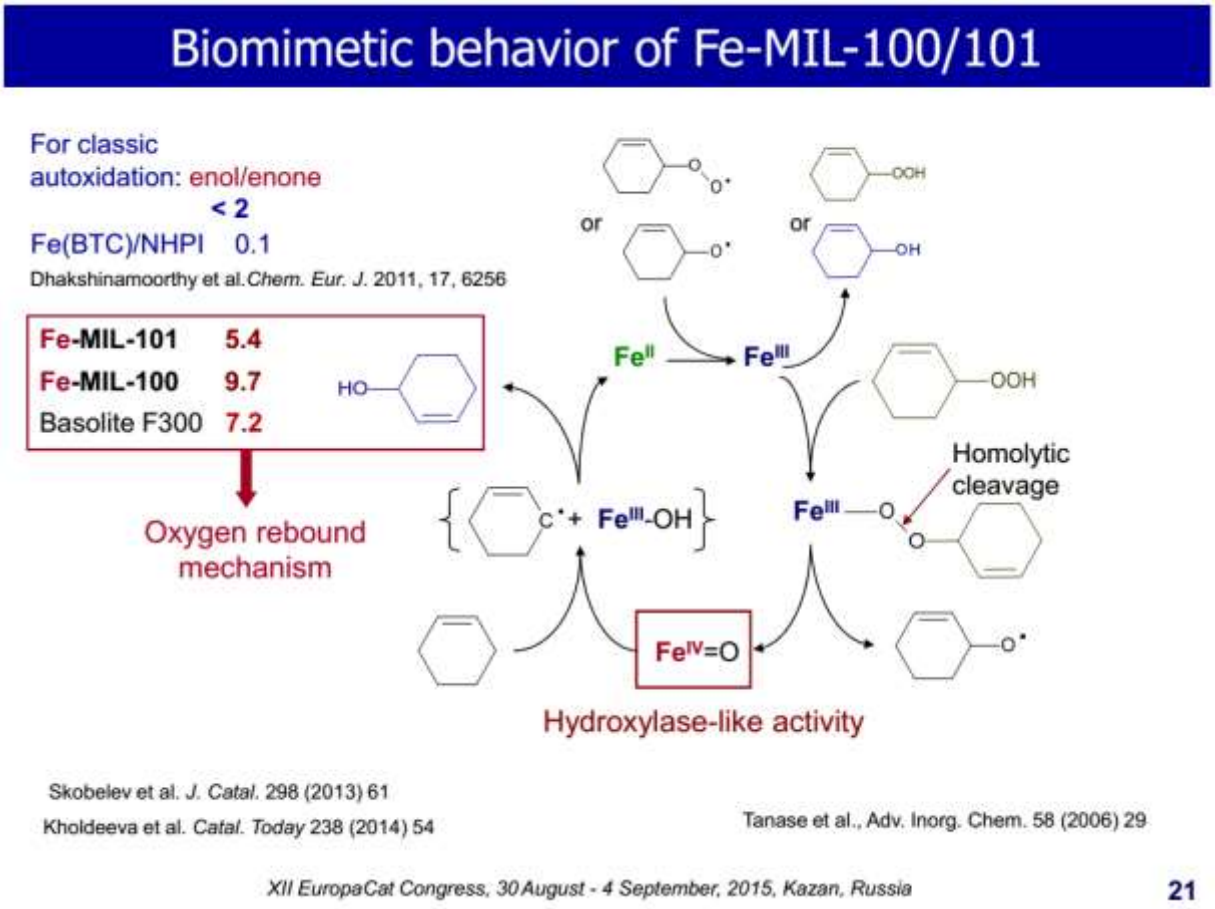


4. **One of the first demonstrations of the successful use of MOFs as heterogeneous catalysts for liquid-phase processes of organic synthesis (selective oxidation of cyclohexane, anthracene, and a range of alkenes; cycloaddition of CO2 to epoxides). Evaluation of stability limits of MOFs and recommendations on the optimal conditions of the catalytic reactions.**

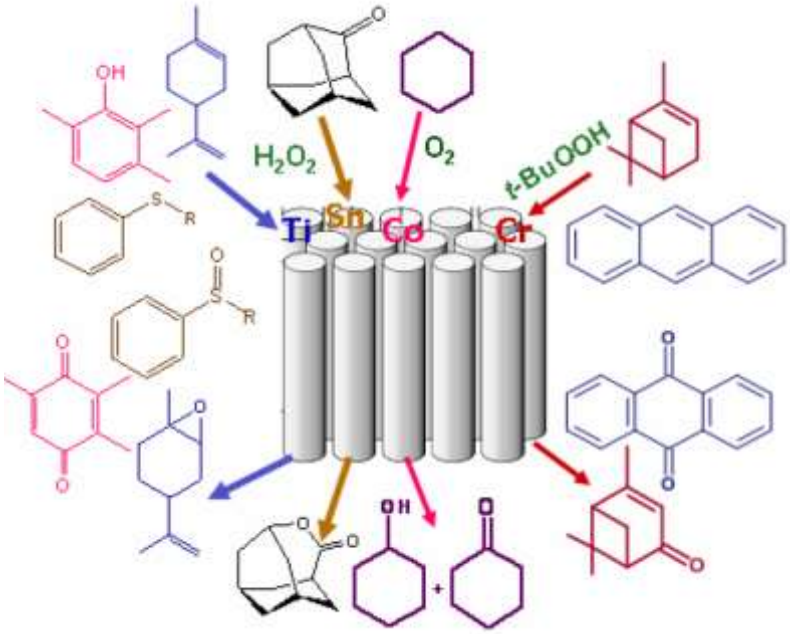
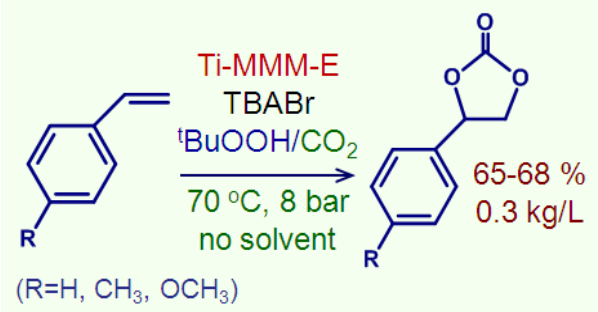
		N. V. Maksimchuk, K. A. Kovalenko, V. P. Fedin, O. A. Kholdeeva, Cyclohexane selective oxidation over metal-organic frameworks of MIL-101 family: superior catalytic activity and selectivity, *Chem. Commun.* 2012, 48 (54), 6812-6814. Collaborative work with the Prof. V.P. Fedin group (NIIC, Novosibirsk)
		O. V. Zalomaeva, A. M. Chibiryaev, K. A. Kovalenko, O. A. Kholdeeva, B. S. Balzhinimaev, V. P. Fedin, Cyclic carbonates synthesis from epoxides and CO_2 over metal-organic framework Cr-MIL-101, *J. Catal.* 2013, 298, 179-185. Collaborative work with the Prof. V.P. Fedin group (NIIC, Novosibirsk)
	Coordination polymer MIL-125 can serve as a precursor for highly active, selective and recyclable heterogeneous catalyst for selective oxidation of substituted phenols to quinones.	I. D. Ivanchikova, J. S. Lee, N. V. Maksimchuk, A. N. Shmakov, Yu. A. Chesalov, A. B. Ayupov, Y. K. Hwang, C.-H. Jun, J.-S. Chang, O. A. Kholdeeva, Highly selective H_2O_2-based oxidation of alkylphenols to *p*-benzoquinones over MIL-125 metal–organic frameworks, *Eur. J. Inorg. Chem.* 2014 (1), 132-139. Collaborative work with the Prof. J.S. Chang (Korea Research Institute of Chemical Technology (KRICT), Republic of Korea)

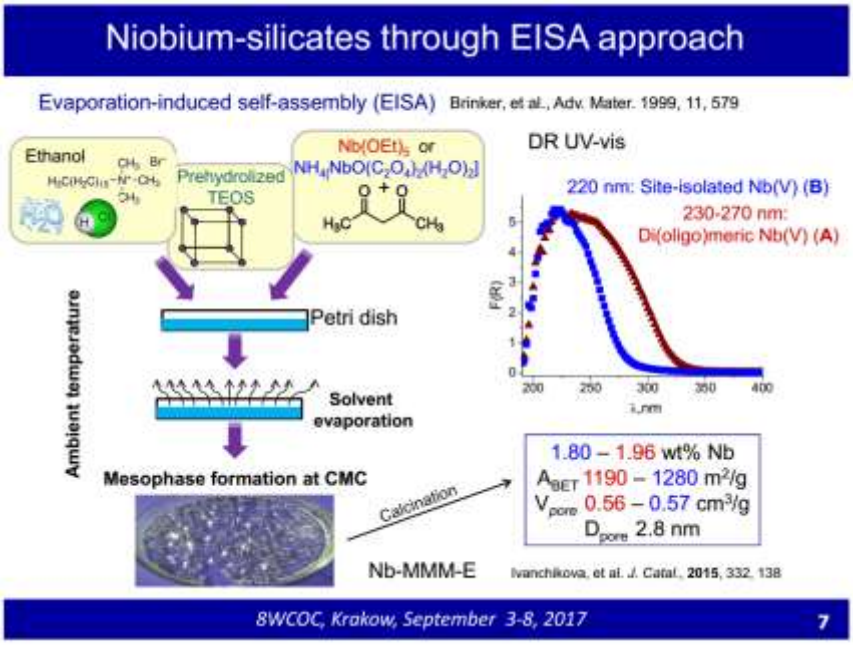
5. **Discovery of a biomimetic behavior of iron-containing MOFs (Fe-MIL-100, MIL-101, FeBTC) in aerobic oxidation of alkenes.**

Collaborative work with the Prof. V.P. Fedin group (NIIC, Novosibirsk)

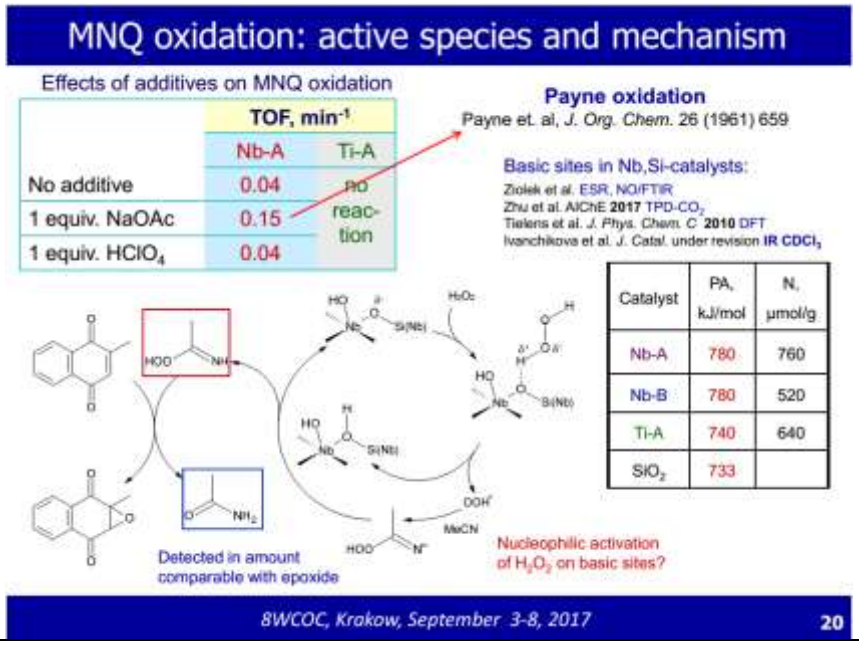


6. **New methods for the synthesis of mesoporous metal-silicates and their use as heterogeneous catalysts for production of valuable products of organic and fine organic synthesis.**

	O. A. Kholdeeva, in *Liquid Phase Oxidation via Heterogeneous Catalysis: Organic Synthesis and Industrial Applications*, eds. M.G. Clerici and O.A. Kholdeeva, JohnWiley & Sons, Inc., Hoboken, New Jersey, **2013**, Ch. 4, p.127-219. O. A. Kholdeeva, Recent developments in liquid-phase selective oxidation using environmentally benign oxidants and mesoporous metal-silicates**,** *Catal. Sci. Technol.*, **2014,** 4 (7), 1869–1889. I. D. Ivanchikova, M. K. Kovalev, M. S. Mel'gunov, A. N. Shmakov, O. A. Kholdeeva. User-friendly synthesis of highly selective and recyclable mesostructured titanium-silicate catalysts for the production of bulky benzoquinones, *Catal. Sci. Technol.*, **2014**, 4 (1), 200–207.
	N.V. Maksimchuk, I.D. Ivanchikova, A. B. Ayupov, O.A. Kholdeeva, One-step solvent-free synthesis of cyclic carbonates by oxidative carboxylation of styrenes over a recyclable Ti-containing catalyst, *Applied Catalysis B: Environmental* **2016**, 181, 363–370.



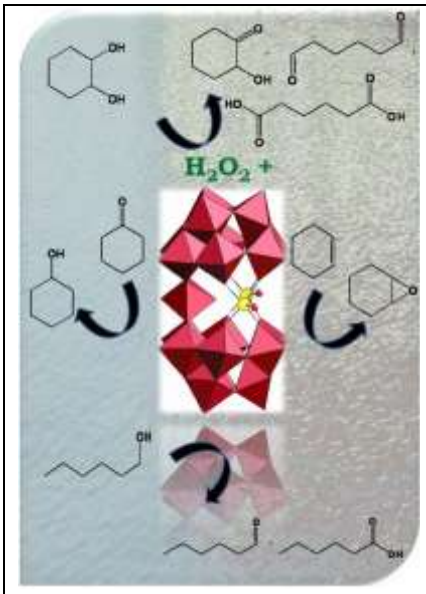
I. D. Ivanchikova, N.V. Maksimchuk, I. Y. Skobelev, O. A. Kholdeeva, Mesoporous niobium–silicates prepared by evaporation–induced self–assembly as catalysts for selective oxidations with aqueous H_2O_2, *J. Catal.*, **2015**, 332, 138–148.

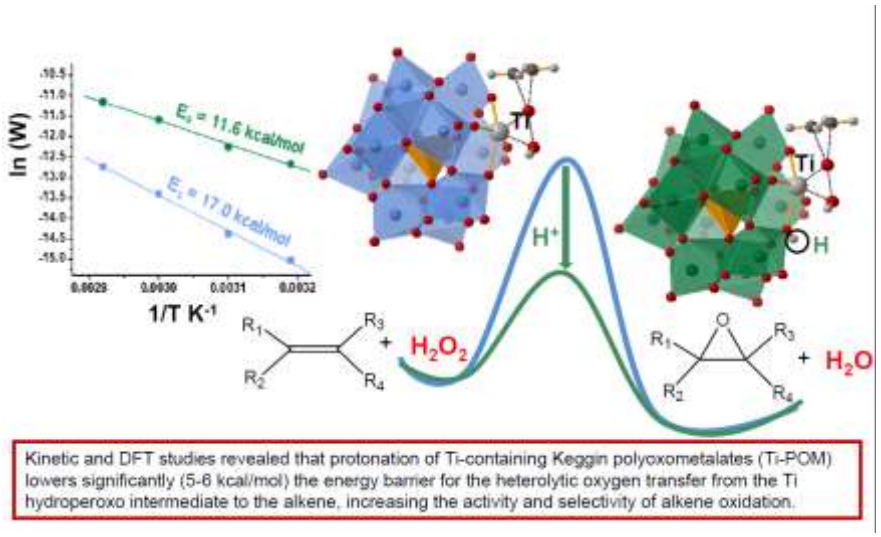


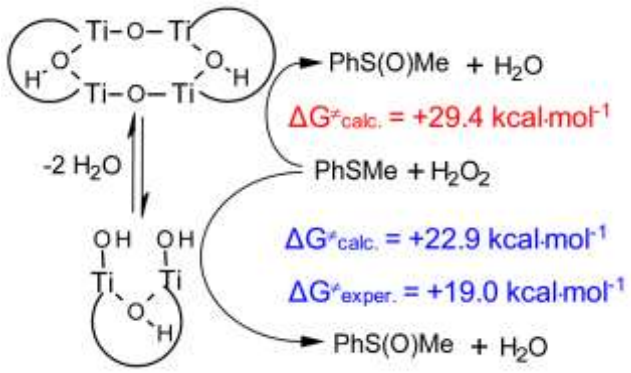
I.D. Ivanchikova, I. Y. Skobelev, N. V. Maksimchuk, E. A. Paukshtis, M. V. Shashkov, O. A. Kholdeeva, Toward understanding the unusual reactivity of Nb-containing catalysts in epoxidation of C=C bonds with hydrogen peroxide. *J. Catal.* **2017**, 356C, 85-99.

8 World Congress on Oxidation Catalysis, 8WCOC, Krakow, 2017, *key-note lecture*

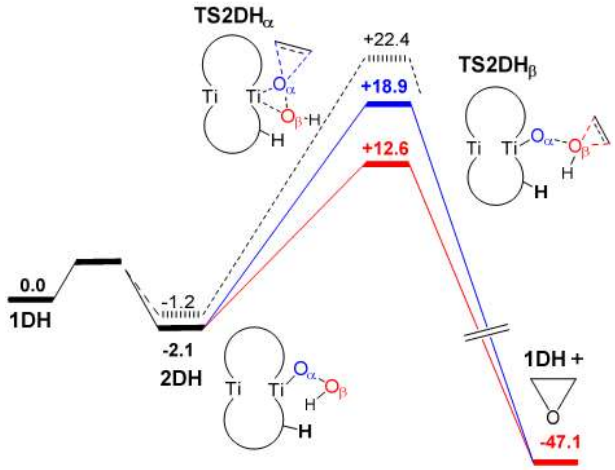
7. Studies on mechanisms of hydrogen peroxide activation and oxidation catalysis using polyoxometalates (POM) as molecular models.

 O. A. Kholdeeva, B.G. Donoeva, T. A. Trubitsina, G. Al-Kadamany, U. Kortz, Unique Catalytic Performance of the Polyoxometalate $[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)]^{8-}$: The Role of 5-Coordinated Titanium in H_2O_2 Activation, *Eur. J. Inorg. Chem.* **2009,** 5134–5141.	Sandwich polyoxometalate $[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)]^{8-}$, revealed a unique ability to activate H_2O_2 via a heterolytic mechanism. This ability is due to the presence of unusual 5-coordinated Ti(IV) in the belt of this POM. O. A. Kholdeeva, Hydrogen peroxide activation over Ti(IV): What have we learned from studies on Ti-containing polyoxometalates, *Eur. J. Inorg. Chem.*, **2013**, 1595–1605. Collaborative work with Prof. U. Kortz (Jacobs International university, Bremen), Prof. J.M. Poblet and Dr. J.J. Carbó (Universitat Rovira i Virgili, Tarragona) This work was supported by a DFG-RFBR grant 09-03-91333	F. Hussain, B. S. Bassil, U. Kortz, O. A. Kholdeeva, M. N. Timofeeva, P. de Oliveira, B. Keita and L. Nadjo, Di-Titanium Containing 19-Tungstodiarsenate(III) $[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)]^{8-}$: Synthesis, Structure, Electrochemistry and Oxidation Catalysis, *Chemistry A European Journal*, **2007**, 13, 4733 - 4742 N. S. Antonova, J. J. Carbó, U. Kortz, O. Kholdeeva, J. M. Poblet, Mechanistic insights into the alkene epoxidation with H_2O_2 by Ti- and other TM-containing polyoxometalates: role of the metal nature and coordination environment, *J. Am. Chem. Soc.*, **2010**, *132*, 7488–7497. B. G. Donoeva, T. A. Trubitsina, N. S. Antonova, J. J. Carbó, J. M. Poblet, G. Al Kadamany, U. Kortz, O. A. Kholdeeva, Epoxidation of alkenes with H_2O_2 catalyzed by di-titanium-containing 19-tungstodiarsenate(III): experimental and theoretical studies, *Eur. J. Inorg. Chem.* **2010,** 5312–5317.

	P. Jiménez-Lozano, I. D. Ivanchikova, O. A. Kholdeeva, J. M. Poblet, and J. J. Carbó, Alkene oxidation by Ti-containing polyoxometalates. Unambiguous characterization of the role of protonation state. *Chem. Commun.* **2012**, 48, 9266-9268. Collaborative work with Prof. J.M. Poblet and Dr. J.J. Carbó (Universitat Rovira i Virgili, Tarragona)



I. Y. Skobelev, O. V. Zalomaeva, O.A. Kholdeeva, J. M. Poblet, J. J. Carbó, Mechanism of thioether oxidation over di- and tetrametic Ti centers: Kinetic and DFT studies based on model Ti-containing polyoxometalates. *Chem. Eur. J.*, **2015**, 21, 14496 –14506.

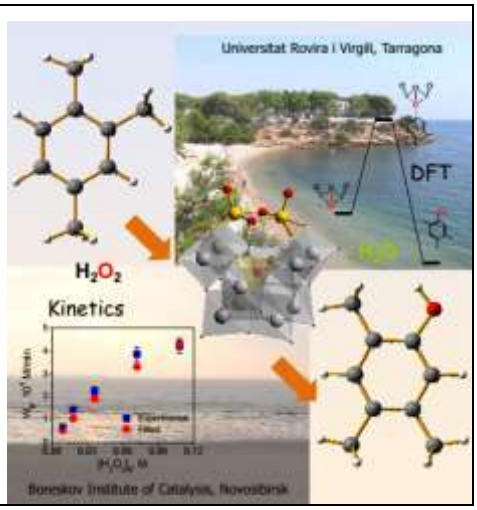


P. Jiménez-Lozano, I. Y. Skobelev, O. A. Kholdeeva, J. M. Poblet, J. J. Carbó, Alkene epoxidation catalyzed by Ti-containing polyoxometalates: Unprecedented β-oxygen transfer mechanism, *Inorg. Chem.*, **2016**, 55 (12), 6080–6084.

Collaborative work with Prof. J.M. Poblet and Dr. J.J. Carbó (Universitat Rovira i Virgili, Tarragona)

Using kinetic, spectroscopic (^{31}P and ^{51}V NMR) and theoretical (DFT) tools, the mechanism of aromatic ring hydroxylation of alkylbenzenes with hydrogen peroxide catalyzed by $(Bu_4N)_4[\gamma\text{-}PW_{10}O_{38}V_2(\mu\text{-}O)(\mu\text{-}OH)]$ has been studied. DFT calculations showed that the steric hindrance exerted by peroxo complex $(Bu_4N)_3[\gamma\text{-}PW_{10}O_{38}V_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)]$ is responsible of the origin of the unusual regioselectivity observed in pseudocumene hydroxylation.

I.Y. Skobelev, V.Yu. Evtushok, O.A. Kholdeeva, N.V. Maksimchuk, R.I. Maksimovskaya, J.M. Ricart, J.M. Poblet, J.J. Carbo, *ACS Catal.*, **2017**, 7, 8514–8523.



8. **Development of efficient techniques for immobilization of polyoxometalates and application of immobilized POMs in liquid-phase selective oxidations.**

Review papers:

O.A. Kholdeeva, N.V. Maksimchuk, G.M. Maksimov, Polyoxometalate-Based Heterogeneous Catalysts for Liquid Phase Selective Oxidations: Comparison of Different Strategies, *Catal. Today,* **2010,** 157, 107–113.

N. V. Maksimchuk, O. A. Kholdeeva, K. A. Kovalenko, V. P. Fedin, MIL-101 Supported Polyoxometalates: Synthesis, Characterization and Catalytic Applications in Selective Liquid-Phase Oxidation, *Israel J. Chem.* **2011**, 2, 281-289.

C. L. Hill, O. A. Kholdeeva, in *Liquid Phase Oxidation via Heterogeneous Catalysis: Organic Synthesis and Industrial Applications*, eds. M.G. Clerici and O.A. Kholdeeva, John Wiley & Sons, Inc., Hoboken, New Jersey, 2013, Ch. 6, p.263-319.

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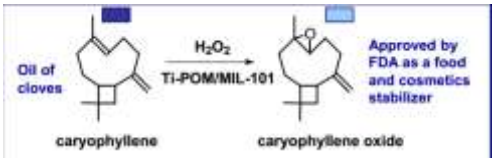

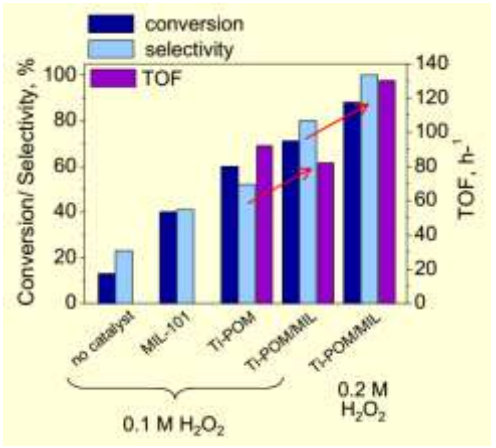

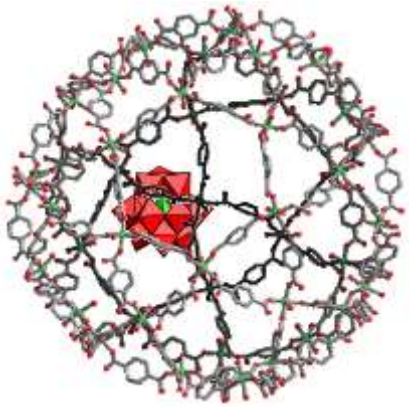
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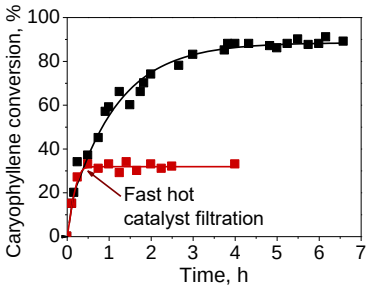
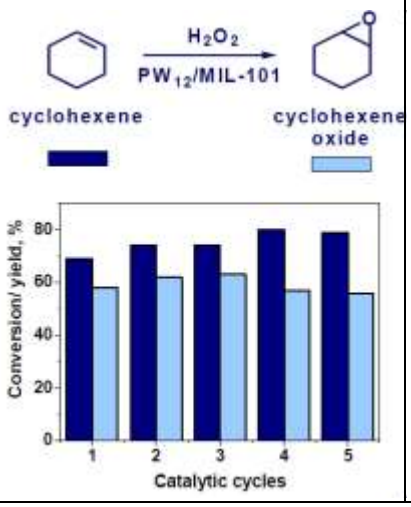


POM immobilization within nanocages of the coordination polymer MIL-101 leads to highly active, selective and truly heterogeneous catalysts for liquid-phase selective oxidations.


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N. V. Maksimchuk, M. N. Timofeeva, M. S. Melgunov, A.N. Shmakov, Yu. A. Chesalov, D. N. Dybtsev, V. P. Fedin, O. A. Kholdeeva, Heterogeneous selective oxidation catalysts based on coordination polymer MIL-101 and transition metal substituted polyoxometalates, *J. Catal*, **2008**, 257, 315–323.

N.V. Maksimchuk, K.A. Kovalenko, S.S. Arzumanov, Yu.A. Chesalov, A.G. Stepanov, V.P. Fedin, and O.A. Kholdeeva, Hybrid polyoxotungstate/MIL-101 materials: Synthesis, Characterization, and Catalysis of H_2O_2-based alkene epoxidation, *Inorg. Chem.*, **2010**, 49 (6), 2920–2930.
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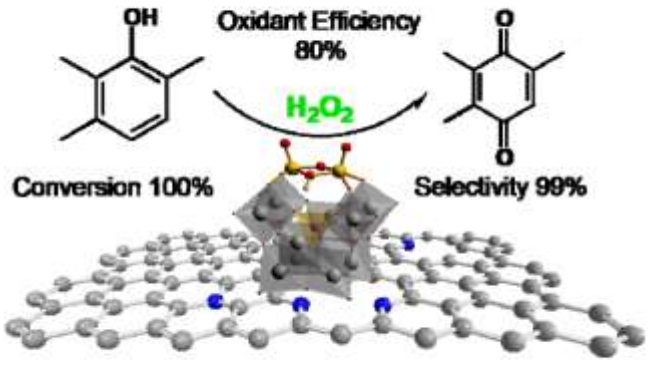
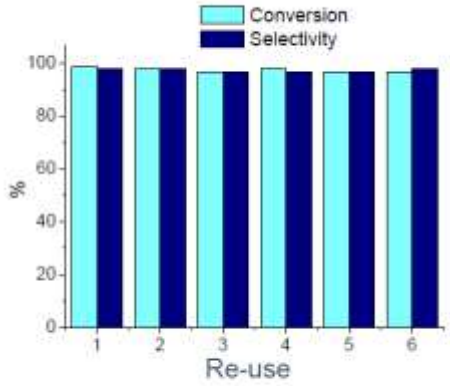
Highly efficient catalyst for production of substituted quinones

A novel approach for the environmentally benign synthesis of alkyl-*p*-benzoquinones, which employs aqueous hydrogen peroxide as green oxidant and a divanadium-substituted γ-Keggin polyoxotungstate, [γ-$PW_{10}O_{38}V_2(\mu\text{-}O)(\mu\text{-}OH)]^{4-}$ (V_2-POM), immobilized on nitrogen-doped carbon nanotubes (N-CNTs) as heterogeneous catalyst, has been suggested. The presence of nitrogen in the support ensures strong adsorption and molecular dispersion of V_2-POM on the carbon surface, leading to highly active and selective heterogeneous catalysts, which do not suffer from metal leaching and can be used repeatedly without loss of the catalytic performance. The catalyst demonstrated truly heterogeneous nature of the catalysis and unprecedentedly high turnover frequencies (500 h^{-1}) and space-time yield (450 g L^{-1} h^{-1}).





V.Yu. Evtushok, A.N. Suboch, O.Yu. Podyacheva, O.A. Stonkus, V. I. Zaikovskii, Yu.A. Chesalov, L.S. Kibis, O.A. Kholdeeva, *ACS Catal.*, **2018**, *8*, 1297−1307