DE GRUYTER Pure Appl. Chem. 2017; 89(8): 1157–1166

Conference paper

Eduard Karakhanov*, Anton Maximov, Maksim Boronoev, Leonid Kulikov
and Maria Terenina

Mesoporous organo-inorganic hybrid materials as hydrogenation catalysts

DOI 10.1515/pac-2016-1207

Abstract: The paper concerns application of two types of organic materials – porous aromatic frameworks (PAFs) with diamond-like structure and the ordered mesoporous phenol-formaldehyde polymers (MPFs) – as supports for metal and metal sulfide nanoparticles. The obtained hybrid materials were tested in hydrogenation of various unsaturated and aromatic compounds. Ruthenium catalyst, based on PAF (Ru-PAF-30), possessed high activity in exhaustive hydrogenation of phenol into cyclohexanol with TOF value of 2700 h^{-1}. Platinum catalyst, based on modified with sulfo-groups MPF (MPF-SO_3H-Pt), was selective in semi-hydrogenation of terpenes, [α-terpinene, γ-terpinene, terpinolene, (s)-limonene]. Bimetallic Ni–W sulfide catalysts, prepared by in situ decomposition of $[(n\text{-Bu})_4N]_2Ni(WS_4)_2$ within the pores of MPFs and PAFs, possessed high efficiency in hydrogenation-hydrocracking of naphthalenes as model substrates.

Keywords: heterogeneous catalysis; hybrid materials; hydrogenation; porous networks; Mendeleev XX; mesoporous materials; nanoparticles.

Introduction

Development of new functional materials that could improve present technologies is of great importance to meet the growing number of challenges related to health, sustainability, and environmental protection. Combination of organic polymers and inorganic materials has led to the exploration of new materials with unique properties and wide spectrum of applications [1–3]. Over the last decades, tremendous progress has been made in the design of heterogeneous catalysts with defined properties [4–6]. The key point here is to apply methods and procedures that allow to predict or, even, to control the structure and composition of catalytic materials. This includes tailoring pore size and structure of supporting materials, building and defining the location of catalytically active sites, control the size of catalysts nanoparticles and, finally, establishing the reaction mechanism at the molecular scale and using it for optimization of catalytic process.

In particular, one of the most convenient approaches to obtain mesoporous materials with controlled properties are template synthesis routes, numerous cross-coupling and self-assembly reactions. The above

---

Article note: A collection of invited papers based on presentations at the XX Mendeleev Congress on General and Applied Chemistry (Mendeleev XX), held in Ekaterinburg, Russia, September 25–30, 2016.

***Corresponding author: Eduard Karakhanov,** Department of Petroleum Chemistry and Organic Catalysis, Moscow State University, 119991 Moscow, Russia, e-mail: kar@petrol.chem.msu.ru
Anton Maximov: Department of Petroleum Chemistry and Organic Catalysis, Moscow State University, 119991 Moscow, Russia; and Institute of Petrochemical Synthesis RAS, 119991 Moscow, Russia
Maksim Boronoev, Leonid Kulikov and Maria Terenina: Department of Petroleum Chemistry and Organic Catalysis, Moscow State University, 119991 Moscow, Russia

mentioned methods have been applied successfully for preparation of different mesoporous inorganic [7–10], carbon-based materials [11–13] and metal-organic frameworks [14, 15].

Besides great progress in the synthesis of mesoporous materials with defined properties, there is still a great issue to create solid catalysts with necessary location and/or configuration of active sites. Although, a number of certain negative processes may arise on the support surface, such as uncontrollable side reactions or surface effects that are difficult to avoid. Moreover, even if the desired catalyst is obtained, the processes of structure degradation, atom migration from metal nanoparticles and the agglomeration of the latter lead to catalyst deactivation.

Hence, development of stable, non-degradable materials with nanoparticle stabilizing properties is of the great interest. Thus, materials based on aromatic units, linked by covalent carbon-carbon bonds, are particularly important due to their robust structure, high stability and possibility of modification with functional groups. So, the present paper describes the application of mesoporous organic–inorganic hybrid materials based on metal and metal sulfide nanoparticles incorporated into the organic matrix of PAFs and MPFs as hydrogenation catalysts.

PAFs as material for hydrogenation catalysts

Porous aromatic frameworks make up relatively new class of carbon-based polymers that consist of aromatic rings linked with each other, in some cases through hub atoms (Fig. 1). Their advantages are high

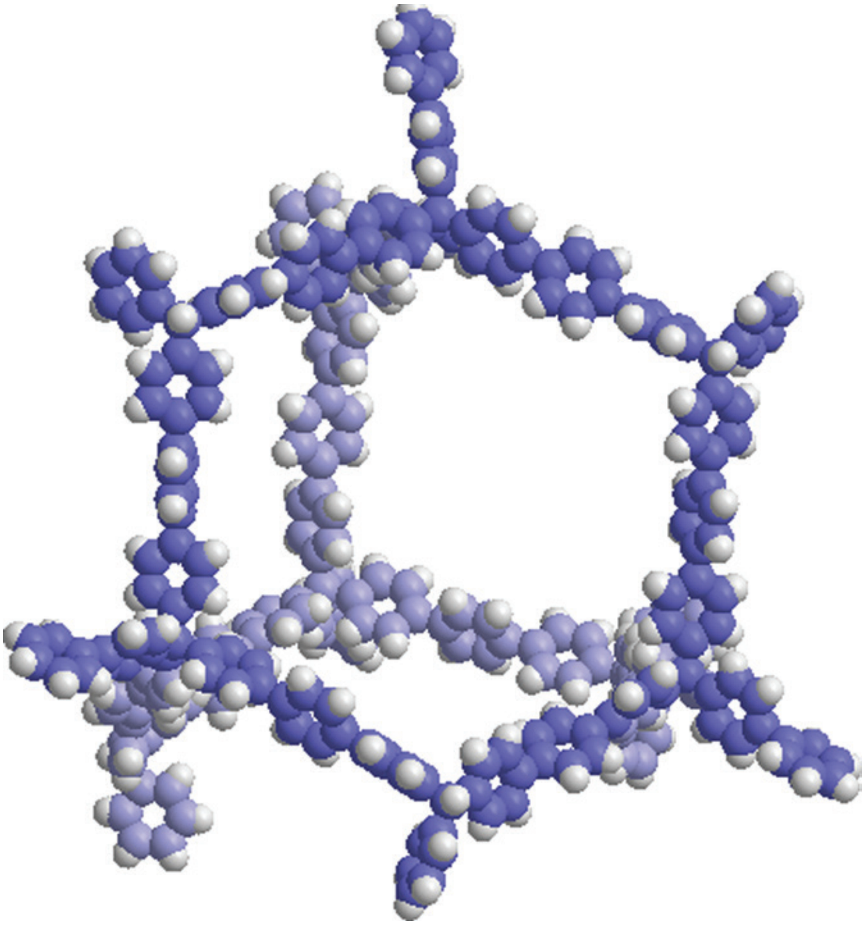


Fig. 1: Representative structure of PAF with *dia* topology on the example of single cell of PAF-20.

surface area, tailored pore sizes, high thermal and chemical stability and diversity of facile functionalization methods. They found application in the fields of gas separation, membrane technology [16–18], and carbon dioxide capture [19–21], as well as materials for light harvesting and catalysis. Talking about the latter application area, porous aromatic frameworks were used for preparation of solid-acid and solid-base catalysts [22–24], catalysts based on immobilized metal complexes [25–27], and classic heterogeneous catalysts with metal nanoparticles within the pores of material [28–32]. Several modifications of the structure make it possible to synthesize materials with ion-exchange properties [21, 25, 32].

In our previous works we reported the synthesis of palladium, platinum and ruthenium nanoparticles within the pores of PAFs [31, 33]. For these purposes PAFs were treated with metal salts in organic solvents ($RuCl_3$ in ethanol with 1,5-cyclooctadiene; $Pd(OAc)_2$ in chloroform; $H_2[PtCl_6]$ in methanol) with subsequent reduction with sodium borohydride to yield the catalysts Ru-PAF-20 (Ru – 3.9 % mass.), Ru-PAF-30 (Ru – 4.8 % mass.), PAF-30-Pt (Pt – 6.0 % mass.) and PAF-30-Pd (Pd – 5.1 % mass.).

The initial PAF materials were synthesized by Suzuki cross-coupling reaction between tetrakis-[p-bromophenyl]methane and 1,4-phenylenediboronic acid or 4,4′-biphenyldiboroic acid. Consequently, corresponding frameworks have *dia* topology and 3 or 4 benzene rings in the edge. The obtained materials consisted of spheres with the diameter of 100–300 nm and displayed high thermal stability (up to 420 °C) and surface area (480 m^2/g for PAF-20 and 300 m^2/g for PAF-30).

The synthesized catalysts were successfully used for hydrogenation of unsaturated compounds. It should be noted that the size-selective effect was observed for these materials. Thus, ruthenium catalyst Ru-PAF-20, based on framework with lesser pore size (PAF-20, three benzene rings in the edge) was active in hydrogenation of only small substrates – benzene, toluene and phenol, whereas Ru-PAF-30 catalyst that is based on PAF with bigger pore size (PAF-30, four benzene rings in the edge) was successfully used for hydrogenation of more bulky compounds – up to tetralin (Fig. 2).

MPFs as material for hydrogenation catalysts

Mesoporous phenol-formaldehyde polymers represent an advanced class of ordered mesoporous materials which combines qualities of both inorganic mesoporous materials and hydrophobic organic supports [13]. Unlike COFs and PAFs with amorphous networks, MPFs possess tunable periodic structures, ordered and uniform mesopores with adjustable mesopore sizes (2–30 nm). These materials have found applications in various processes as supports for immobilization of metal nanoparticles [34–38], metal complexes [39–41], ionic liquids [42–44], and as solid base [45, 46] or acid [47–49] catalysts.

Different variations of MPF synthesis methods have been developed over the past decade [50–54]. The general procedure of mesoporous phenol-formaldehyde polymers synthesis is based on a solvent evaporation induced self-assembly method (EISA), which implies using amphiphilic triblock copolymer (Pluronic F127) as template, and a soluble low-molecular weight polymer of phenol and formaldehyde (resol) as a precursor, followed by thermopolymerization process at 100 °C for 24 h and template removal at 350 °C under inert atmosphere. The obtained mesoporous polymers possess a hexagonal mesostructure with channel like pores and a high surface area (350–600 m^2/g).

The abundance of aromatic rings in MPF polymeric networks provides abilities for introduction of functional groups into the structure. A series of mesoporous phenolic resin-based catalysts has been developed by chemical modification of organic framework walls [13]. Modification with functional groups makes it possible to immobilize metal ions, to stabilize nanoparticles, and to ensure their regular incorporation into the pore space (Fig. 3). In addition, these groups can serve as surface modifiers of transition metal nanoparticles and influence the activity and selectivity of catalysts [55–57]. Thus, the development of catalysts based on metal nanoparticles stabilized by the π-electrons of benzene ring moieties and additional functional groups is of great interest.

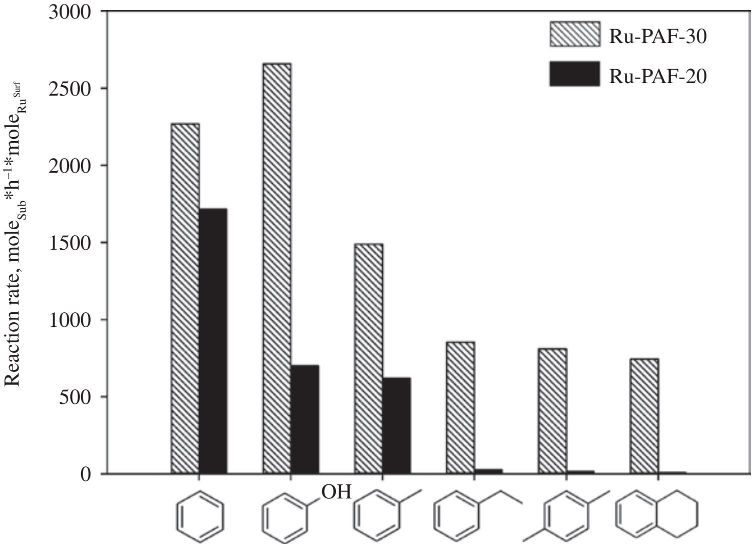


Fig. 2: Hydrogenation of arenes in presence of Ru-PAF-20 and Ru-PAF-30. Reaction conditions: 80 °C, 3.0 MPa H_2, 1 h, 3 mg cat., $V(H_2O) = V(sub.)$; substrate:metal = 2000:1 mol. Reprinted from [31].

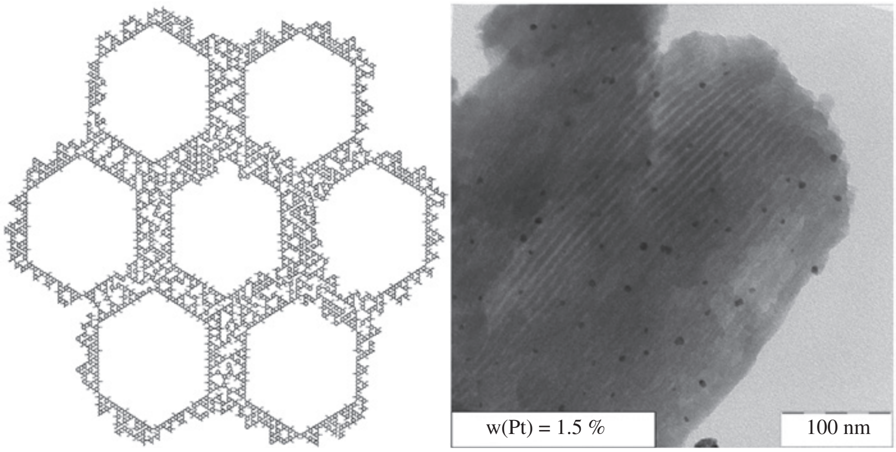
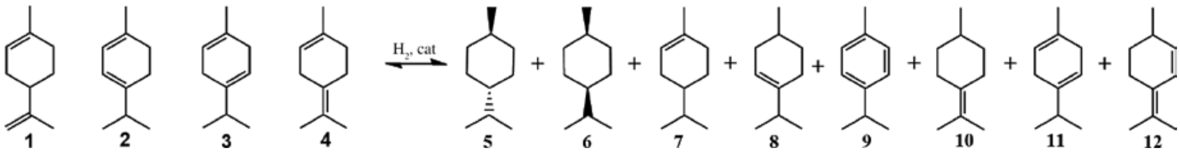


Fig. 3: Representative structure of mesoporous phenol-formaldehyde polymer (on the left) and TEM image of MPF-SO_3H-Pt-c catalyst (on the right).

In the recent work, we described encapsulation of platinum and palladium nanoparticles in mesoporous phenol-formaldehyde resins, modified with sulfo groups, and application of synthesized catalysts in hydrogenation of terpenes (Scheme 1, Fig. 4) [38]. Palladium catalysts showed high activity in exhaustive hydrogenation, whereas platinum catalysts exhibited unexpected selectivity towards monoenes. It is assumed that metal and hydroxyl oxygen of the sulfo group undergo a Coulomb interaction, which results in electron



Scheme 1: Hydrogenation of (s)-limonene, α-terpinene, γ-terpinene and terpinolene.

transfer from metal to oxygen [58]. In consequence, the resulting monoene much more readily undergoes readsorption and hydrogenation on the electron depleted Pd surface.

PAF and MPF as supports for noble metal catalysts

The development of highly active and selective hydrogenation catalysts capable of converting acetylenes to alkenes without a significant increase in the alkane content is a problem of considerable interest [59, 60]. In this connection, different approaches such as poisoning, using metal oxides, metal alloys, hybrid, and single-site catalysts can be applied. Metal nanoparticles immobilized in polymeric supports with a regular structure are one of the most attractive types of catalysts for reactions in conventional flow reactors, and for use in slurry phase systems [61–63].

Catalysts based on palladium and platinum nanoparticles supported on the porous aromatic frameworks and mesoporous phenol-formaldehyde resin modified with sulpho groups and PPI dendrimers were used in hydrogenation of several unsaturated compounds (Figs. 5–8) [33, 35, 36]. The size of metal nanoparticles was estimated to be in the range of 3.2–5.3 nm and was slightly higher for platinum. It was found that Pt-PAF-30 catalyst was more active, but the selectivity was higher for Pd-PAF-30 catalyst in semihydrogenation of phenylacetylene and 2,5-dimethyl-2,4-hexadiene (Fig. 6). These results are in accordance with numerous works, reported earlier [64, 65]. Alternatively, Pd-containing catalysts modified with sulfo groups exhibited higher activity than platinum catalysts. It is assumed that in case of sulfonated Pt catalysts, a special synergetic effect occurs between metal and SO_3^- groups, which is responsible for activity and selectivity [36]. All catalysts showed high selectivity (not less than 92 %) for styrene in phenylacetylene hydrogenation. Besides,

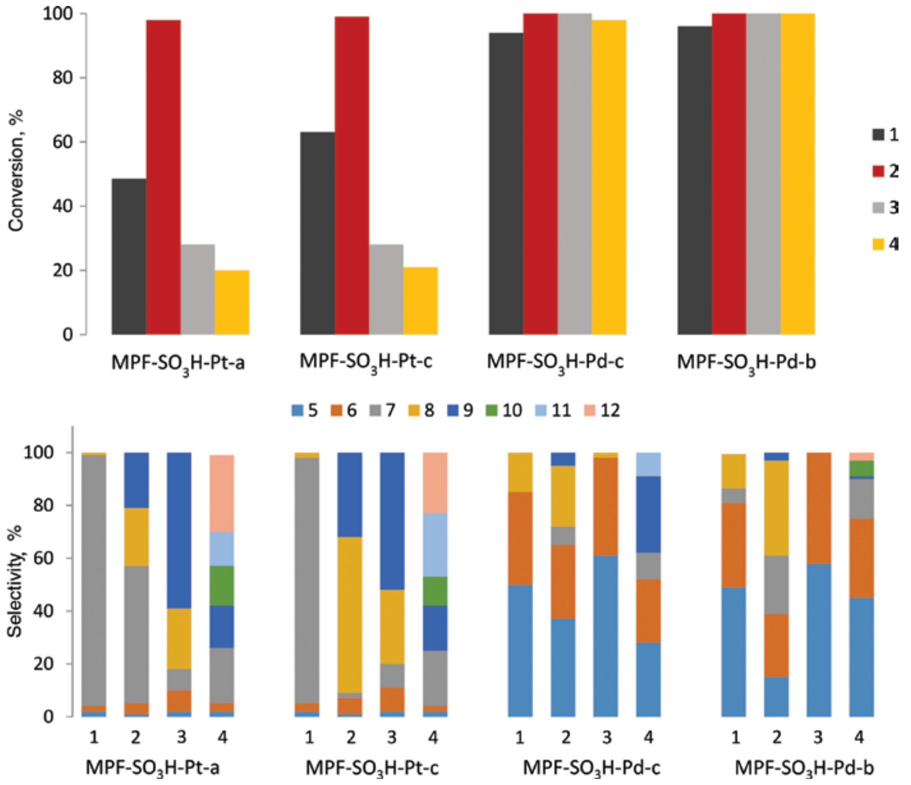


Fig. 4: Conversion and product selectivity distribution for the terpenes hydrogenation. Reaction conditions: 80 °C, 4.0 MPa H_2, 1 h, substrate/metal = 1500–4000 mol.

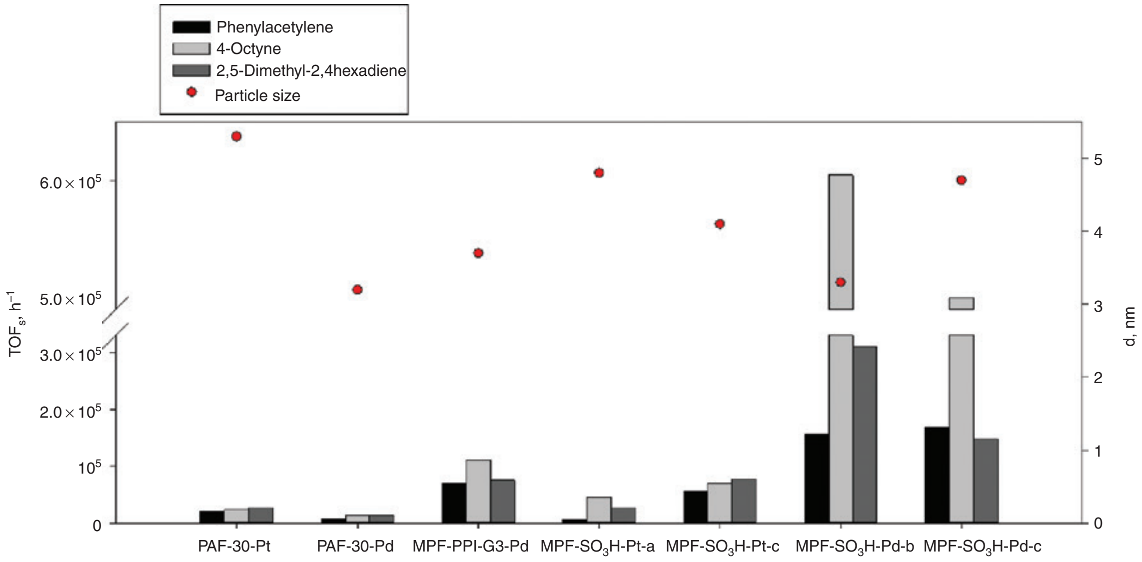


Fig. 5: Catalytic activity of noble metal catalysts in hydrogenation of unsaturated hydrocarbons. Reaction conditions: (a) 60 °C, 1.0 MPa H_2, 30 min, substrate/metal = 27 000 mol/mol (PAF-30-Pt, PAF-30-Pd); (b) 80 °C, 1.0 MPa H_2, 15 min, substrate/metal = 8000–65 000 mol/mol (MPF-PPI-G3-Pd, MPF-SO$_3$H-Pt-a, MPF-SO$_3$H-Pt-c, MPF-SO$_3$H-Pd-b, MPF-SO$_3$H-Pd-c).

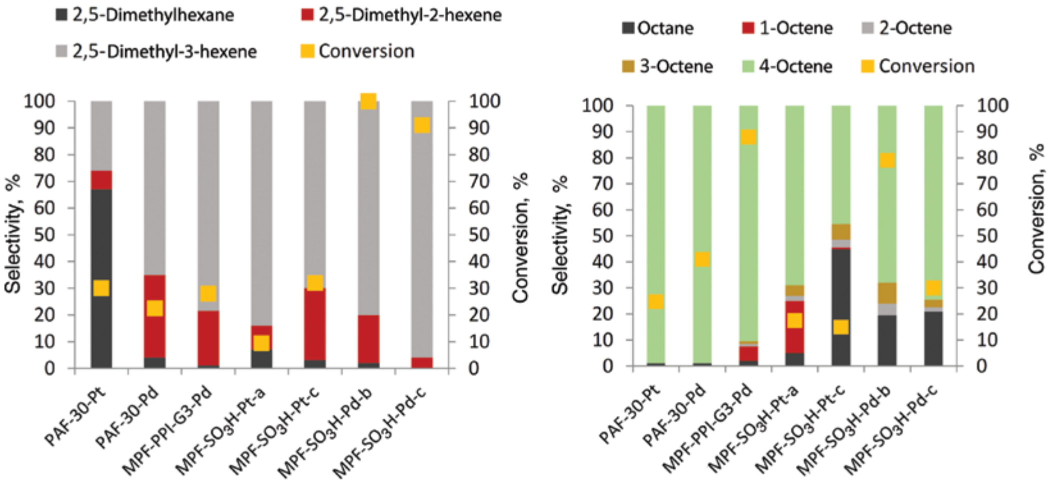


Fig. 6: Product selectivity distribution and conversion in hydrogenation of 2,5-dimethyl-2,4-hexadiene and 4-octyne.

in case of dendrimer-modified catalyst MPF-PPI-G3-Pd high selectivity for semi-hydrogenated products was retained until the complete substrate conversion [37].

PAF and MPF as supports for sulfide catalysts

All catalysts above were active in hydrogenation of comparably small substrates. However, one of the challenges of current industry is conversion of high-boiling hydrocarbons into fuels, or, in other words, into hydrocarbons with lower molecular weight and higher H to C value. In general, this process can be divided into two steps: hydrogenation of unsaturated bonds and subsequent cracking of some saturated bonds. Although noble metal-based catalysts possess high hydrogenation activity, they are extremely sensitive to

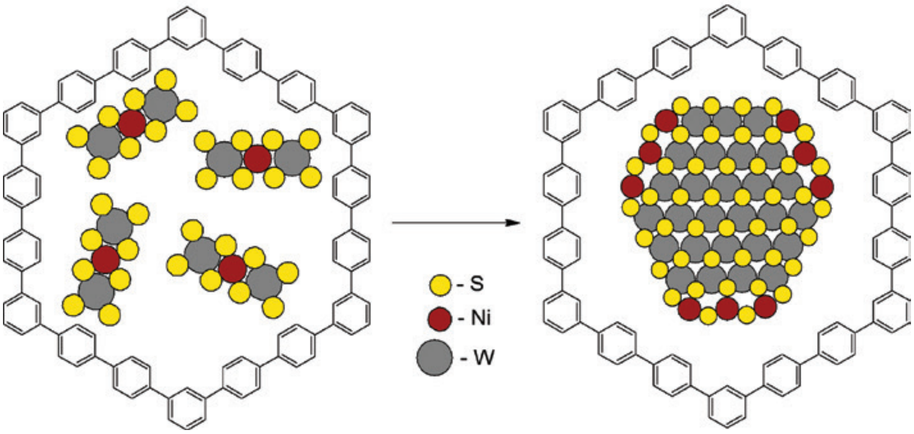


Fig. 7: Scheme of NiWS-phase formation from thiosalt within the pores of polymers.

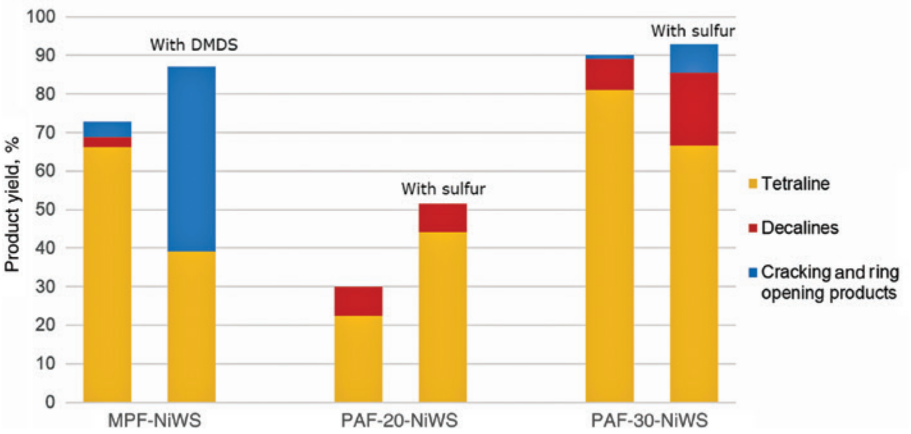


Fig. 8: Naphthalene hydrogenation over NiWS catalysts. Reaction conditions: 380 °C, 5.0 MPa H_2, 5 h, 50 mg cat., 50 mg of sulfur and 2 mL of benzene for PAF-based catalysts, 70 µL DMDS and 2 mL of $C_{16}H_{34}$ for MPF-based catalyst, 80 mg of naphthalene.

the presence of catalytic poisons, especially to different sulfur-containing compounds [66]. This fact makes it difficult to use noble metal-based catalysts in hydrogenation of high-boiling compounds, because in most cases they contain impurities such as numerous substituted dibenzothiophenes, benzothiophenes, thiols, sulfoxides, etc.

A number of catalysts stable in the presence of sulfur-containing compounds include molybdenum and tungsten sulfides, often with addition of promoting elements – nickel or cobalt [67, 68]. There is a great variety of synthesis methods of such catalysts, which differ in starting materials, conditions of MeS_2 phase formation, and applied promoter [69–73].

Our approach was to obtain active sulfide phase in situ during the reaction. The general procedure includes infiltration of PAFs or MPF with $[(n\text{-}Bu)_4N]_2Ni(WS_4)_2$ and further decomposition of the salt to form NiWS phase in the course of the reaction (Fig. 7).

The synthesis details of this approach have been reported recently [74, 75]: tungsten catalysts with metal content of 15 % wt., based on PAF and MPF, were obtained and tested in the hydrogenation-hydrocracking reactions of naphthalene and methylnaphthalenes as model substrates. The combined results of the experiments are presented in Figs. 8 and 9.

The highest conversions of naphthalene into reaction products using PAF-based catalysts were achieved using sulfurizing agents. To give an explanation to these results, analysis of the catalysts structure after the

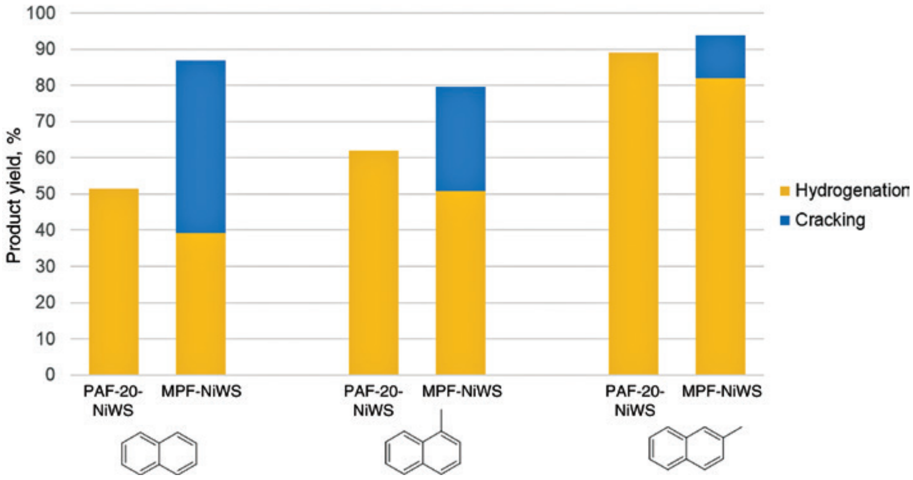


Fig. 9: Hydrogenation of naphthalenes over NiWS catalysts. Reaction conditions: 380 °C, 5.0 MPa H_2, 5 h, 50 mg cat., 50 mg of sulfur and 2 mL of benzene for PAF-based catalyst, 70 µL DMDS and 2 mL of $C_{16}H_{34}$ for MPF-based catalyst, 80 mg of naphthalene or 90 mg of methylnaphthalenes.

reaction was performed. The XPS study of the catalysts revealed, that without sulfurizing agent the predominant metal form is W^{6+}, whereas the addition of sulfur and DMDS leads to higher shares of WS_2 form, which is more active in hydrogenation than the former phase.

PAF-NiWS catalytic systems possessed very low cracking performance. This fact can be attributed to the mechanism of catalytic cracking process: the C–C cracking and skeletal isomerization reactions take place in the presence of acids, and therefore, low cracking activity of PAF-NiWS systems is due to the absence of acid sites in the PAF structure and low acidity of NiWS phases. In contrast, in case of MPF-NiWS catalyst, the share of hydrocracking products was up to 35 %. The probable reason of such high cracking activity of MPF-NiWS catalyst is moderate acidity of hydroxy-groups at the reaction conditions. This fact shows a direct impact of functional groups on material properties and, eventually, on the performance of catalysts.

Conclusions

Mesoporous organic-inorganic hybrid materials, based on PAFs and MPFs, were used in hydrogenation of various unsaturated compounds. It was shown, that the presence of functional groups on the surface of mesostructure, pore volume and pore diameter influenced on the catalytic activity of materials. The difference in pore diameters in PAF-based ruthenium catalysts sufficiently impact on the conversion of 'bulky' substrates in hydrogenation reaction, and modification of MPF with functional groups of different nature make possible to control the activity and selectivity of the catalysts. These materials, due to their robust structure, high stability, possibility of modification with functional groups and nanoparticle stabilizing properties, are of considerable interest for creation of new catalysts for different processes.

Acknowledgments: This work was supported by the Russian Science Foundation, project no. 15-19-00099.

References

[1] T. Saegusa. *Pure Appl. Chem.* **67**, 1965 (1995).
[2] J. Pyun, K. Matyjaszewski. *Chem. Mater.* **13**, 3436 (2001).
[3] C. Sanchez, K. J. Shea, S. Kitagawa, C. Sanchez, F. Ribot. *Chem. Soc. Rev.* **40**, 471 (2011).
[4] R. Schlögl. *Angew. Chem. Int. Ed.* **54**, 3465 (2015).

[5] Q. Sun, Z. Dai, X. Meng, F.-S. Xiao. *Chem. Soc. Rev.* **44**, 6018 (2015).
[6] F. Zaera. *Chem. Soc. Rev.* **2**, 2746 (2013).
[7] Y. Wan, D. Zhao. *Chem. Rev.* **107**, 2821 (2007).
[8] R. Zhang, A. A. Elzatahry, S. S. Al-Deyab, D. Zhao. *Nano Today* **7**, 344 (2012).
[9] E. R. Naranov, A. S. Badeeva, A. A. Sadovnikov, S. V. Kardashev, A. L. Maksimov, S. V. Lysenko, V. A. Vinokurov, E. A. Karakhanov. *Pet. Chem.* **56**, 599 (2016).
[10] G. Duan, C. Zhang, A. Li, X. Yang, L. Lu, X. Wang. *Nanoscale Res. Lett.* **3**, 118 (2008).
[11] Y. Yuan, F. Sun, H. Ren, X. Jing, W. Wang, H. Ma, H. Zhao, G. Zhu. *J. Mater. Chem.* **21**, 13498 (2011).
[12] H. Yang, Y. Du, S. Wan, G. D. Trahan, Y. Jin, W. Zhang. *Chem. Sci.* **6**, 4049 (2015).
[13] I. Muylaert, A. Verberckmoes, J. De Decker, P. Van Der Voort. *Adv. Colloid Interface Sci.* **175**, 39 (2012).
[14] W. Xuan, C. Zhu, Y. Liu, Y. Cui. *Chem. Soc. Rev.* **41**, 1677 (2012).
[15] J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp. *Chem. Soc. Rev.* **38**, 1450 (2009).
[16] C. H. Lau, K. Konstas, A. W. Thornton, A. C. Y. Liu, S. Mudie, D. F. Kennedy, S. C. Howard, A. J. Hill, M. R. Hill. *Angew. Chem. Int. Ed. Engl.* **54**, 2669 (2015).
[17] A. V. Volkov, D. S. Bakhtin, L. A. Kulikov, M. V. Terenina, G. S. Golubev, G. N. Bondarenko, S. A. Legkov, G. A. Shandryuk, V. V. Volkov, V. S. Khotimskiy, A. A. Belogorlov, A. L. Maksimov, E. A. Karakhanov. *J. Memb. Sci.* **517**, 80 (2016).
[18] T. Mitra, R. S. Bhavsar, D. J. Adams, P. M. Budd, A. I. Cooper. *Chem. Commun.* **52**, 5581 (2016).
[19] T. Ben, C. Pei, D. Zhang, J. Xu, F. Deng, X. Jing, S. Qiu. *Energy Environ. Sci.* **4**, 3991 (2011).
[20] W. Lu, J. P. Sculley, D. Yuan, R. Krishna, Z. Wei, H.-C. Zhou. *Angew. Chem. Int. Ed.* **51**, 7480 (2012).
[21] W. Lu, D. Yuan, J. Sculley, D. Zhao, R. Krishna, H.-C. Zhou. *J. Am. Chem. Soc.* **133**, 18126 (2011).
[22] Y. Zhang, B. Li, S. Ma. *Chem. Commun.* **50**, 8507 (2014).
[23] E. Merino, E. Verde-Sesto, E. M. Maya, A. Corma, M. Iglesias, F. Sánchez. *Appl. Catal. A Gen.* **469**, 206 (2014).
[24] M. G. Goesten, À. Szécsényi, M. F. de Lange, A. V. Bavykina, K. B. S. S. Gupta, F. Kapteijn, J. Gascon. *ChemCatChem* **8**, 961 (2016).
[25] L. Li, C. Cui, W. Su, Y. Wang, R. Wang. *Nano Res.* **9**, 779 (2016).
[26] J. Fritsch, F. Drache, G. Nickerl, W. Böhlmann, S. Kaskel. *Microporous Mesoporous Mater.* **172**, 167 (2013).
[27] E. Verde-Sesto, E. Merino, E. Rangel-Rangel, A. Corma, M. Iglesias, F. Sánchez. *ACS Sustain. Chem. Eng.* **4**, 1078 (2016).
[28] Q. Zhang, Y. Yang, S. Zhang. *Chem.-A Eur. J.* **19**, 10024 (2013).
[29] A. T. E. Vilian, P. Puthiaraj, C. H. Kwak, S. R. Choe, Y. S. Huh, W.-S. Ahn, Y.-K. Han. *Electrochim. Acta* **216**, 181 (2016).
[30] A. T. E. Vilian, P. Puthiaraj, C. H. Kwak, S.-K. Hwang, Y. S. Huh, W.-S. Ahn, Y.-K. Han. *ACS Appl. Mater. Interfaces* **8**, 12740 (2016).
[31] A. Maximov, A. Zolotukhina, L. Kulikov, Yu Kardasheva, E. Karakhanov. *React. Kinet. Mech. Catal.* **117**, 729 (2016).
[32] Q. Zhang, S. Zhang, S. Li. *Macromolecules* **45**, 2981 (2012).
[33] L. A. Kulikov, M. V. Terenina, I. Y. Kryazheva, E. A. Karakhanov. *Pet. Chem.* **57**, 222 (2017).
[34] R. Xing, Y. Liu, H. Wu. *Chem. Commun.* 6297 (2008). doi: 10.1039/B815186E.
[35] X. Liu, R. Jin, D. Chen, L. Chen, S. Xing, H. Xing, Y. Xing, Z. Su. *J. Mater. Chem. A* **3**, 4307 (2015).
[36] M. P. Boronoev, E. S. Subbotina, A. A. Kurmaeva, Y. S. Kardasheva, A. L. Maksimov, E. A. Karakhanov. *Pet. Chem.* **56**, 109 (2016).
[37] M. P. Boronoev, A. V. Zolotukhina, V. I. Ignatyeva, M. V. Terenina, A. L. Maximov, E. A. Karakhanov. *Macromol. Symp.* **363**, 57 (2016).
[38] E. A. Karakhanov, M. P. Boronoev, E. S. Subbotina, A. V. Zolotukhina, Y. S. Kardasheva, A. L. Maksimov, T. Y. Filippova. *Pet. Chem.* **56**, 1114 (2016).
[39] R. Xing, L. Wu, Z. Fei, P. Wu. J. *Mol. Catal. A Chem.* **371**, 15 (2013).
[40] J. De Decker, T. Bogaerts, I. Muylaert, S. Delahaye, F. Lynen, V. Van Speybroeck, A. Verberckmoes, P. Van Der Voort. *Mater. Chem. Phys.* **141**, 967 (2013).
[41] F. Zhang, X. Yang, F. Zhu, J. Huang, W. He, W. Wang, H. Li. *Chem. Sci.* **3**, 476 (2012).
[42] W. Zhang, Q. Wang, H. Wu, P. Wu, M. He. *Green Chem.* **16**, 4767 (2014).
[43] W. Zhang, T. Liu, H. Wu, P. Wu, M. He. *Chem. Commun.* **51**, 1 (2014).
[44] I. Noshadi, B. Kanjilal, S. Du, G. M. Bollas, S. L. Suib, A. Provatas, F. Liu, R. S. Parnas. *Appl. Energy* **129**, 112 (2014).
[45] S. Yan, Y. Gao, R. Xing, Y. Shen, Y. Liu, P. Wu, H. Wu. *Tetrahedron* **64**, 6294 (2008).
[46] R. Xing, H. Wu, X. Li, Z. Zhao, Y. Liu, L. Chen, P. Wu. *J. Mater. Chem.* **19**, 4004 (2009).
[47] I. Muylaert, A. Verberckmoes, J. Spileers, A. Demuynck, L. Peng, F. De Clippel, B. Sels, P. Van Der Voort. *Mater. Chem. Phys.* **138**, 131 (2013).
[48] R. Xing, N. Liu, Y. Liu, H. Wu, Y. Jiang, L. Chen, M. He, P. Wu. *Adv. Funct. Mater.* **17**, 2455 (2007).
[49] L. Fang, R. Xing, H. Wu, X. Li, Y. Liu, P. Wu. *Sci. China Chem.* **53**, 1481 (2010).
[50] Y. Liang, R. Fu, D. Wu. *ACS Nano* **7**, 1748 (2013).
[51] Y. Liang, S. Lu, D. Wu, B. Sun, F. Xu, R. Fu. *J. Mater. Chem. A* **1**, 3061 (2013).
[52] J. Xu, A. Wang, T. Zhang. *Carbon* **50**, 1807 (2012).
[53] J. Zhang, Z. A. Qiao, S. M. Mahurin, X. Jiang, S. H. Chai, H. Lu, K. Nelson, S. Dai. *Angew. Chem. Int. Ed.* **54**, 4582 (2015).
[54] F. Liu, Q. Wu, C. Liu, C. Qi, K. Huang, A. Zheng, S. Dai. *ChemSusChem* **9**, 2496 (2016).

[55] T. Mallat, A. Baiker. *Appl. Catal. A Gen.* **200**, 3 (2000).

[56] M. García-Mota, J. Gómez-Díaz, G. Novell-Leruth, C. Vargas-Fuentes, L. Bellarosa, B. Bridier, J. Pérez-Ramírez, N. López. *Theor. Chem. Acc.* **128**, 663 (2011).

[57] E. Karakhanov, A. Maximov, Y. Kardasheva, V. Semernina, A. Zolotukhina, A. Ivanov, G. Abbott, E. Rosenberg, V. Vinokurov. *ACS Appl. Mater. Interfaces* **6**, 8807 (2014).

[58] T. Seki, J.-D. Grunwaldt, N. van Vegten, A. Baiker. *Adv. Synth. Catal.* **350**, 691 (2008).

[59] S. A. Nikolaev, L. N. Zanaveskin, V. V Smirnov, V. A. Averyanov, K. L. Zanaveskin. *Russ. Chem. Rev.* **78**, 231 (2009).

[60] G. Vilé, D. Albani, N. Almora-Barrios, N. López, J. Pérez-Ramírez. *ChemCatChem* **8**, 21 (2016).

[61] S. Sarkar, E. Guibal, F. Quignard, A. K. SenGupta. *J. Nanoparticle Res.* **14**, 715 (2012).

[62] S. Mahouche-Chergui, M. Guerrouache, B. Carbonnier, M. M. Chehimi. *Colloids Surfaces A Physicochem. Eng. Asp.* **439**, 43 (2013).

[63] E. A. Karakhanov, A. L. Maksimov, A. V. Zolotukhina, Y. S. Kardasheva. *Russ. Chem. Bull.* **62**, 1465 (2013).

[64] A. K. Talukdar, K. G. Bhattacharyya, S. Sivasanker. *Appl. Catal. A Gen.* **96**, 229 (1993).

[65] G. Carturan, G. Cocco, G. Facchin, G. Navazio. *J. Mol. Catal.* **26**, 375 (1984).

[66] S. V. Lysenko, S. V. Baranova, A. L. Maksimov, S. V. Kardashev, A. B. Kulikov, S. I. Shirokopoyas, V. A. Ostroumova, N. Y. Petrov, E. A. Karakhanov. *Pet. Chem.* **53**, 97 (2013).

[67] J. V. Lauritsen, M. Nyberg, J. K. Nørskov, B. S. Clausen, H. Topsøe, E. Lægsgaard, F. Besenbacher. *J. Catal.* **224**, 94 (2004).

[68] P. P. Minaev, P. A. Nikulshin, M. S. Kulikova, A. A. Pimerzin, V. M. Kogan. *Appl. Catal. A Gen.* **505**, 456 (2015).

[69] B. Hinnemann, J. K. Nørskov, H. Topsøe. *J. Phys. Chem. B* **109**, 2245 (2004).

[70] J. P. R. Vissers, B. Scheffer, V. H. J. de Beer, J. A. Moulijn, R. Prins. *J. Catal.* **105**, 277 (1987).

[71] R. P. Dutta, H. H. Schobert. *Catal. Today* **31**, 65 (1996).

[72] S. G. A. Ferraz, F. M. Z. Zotin, L. R. R. Araujo, J. L. Zotin. *Appl. Catal. A Gen.* **384**, 51 (2010).

[73] I. A. Sizova, A. B. Kulikov, M. I. Onishchenko, S. I. Serdyukov, A. L. Maksimov. *Pet. Chem.* **56**, 44 (2016).

[74] E. Karakhanov, M. Boronoev, V. Ignatyeva, A. Maximov, T. Filippova, Y. Kardasheva. *J. Inorg. Organomet. Polym. Mater.* **26**, 1253 (2016).

[75] E. A. Karakhanov, L. A. Kulikov, A. L. Maximov, A. V Zolotukhina, M. A. Vinnikova, A. O. Ivanov. *Catalysts* **6**, 122 (2016).