
REVIEWS

Oxidative Desulfurization of Hydrocarbon Feedstock

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Abstract—Papers published in the past decade on oxidative desulfurization of hydrocarbon raw materials using hydrogen peroxide, oxygen, and ozone as oxidants, and also using ultrasonic treatment and adsorption and extraction methods for separating the oxidized sulfur-containing compounds are summarized and systematized.

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As various kinds of hydrocarbon raw materials with high sulfur content become involved in processing and as the regulations concerning sulfur content of commercial petroleum products become more stringent, improvement of methods for efficient reduction of the sulfur content of hydrocarbon fractions becomes a pressing problem of the oil-refining industry. Sulfur-containing compounds present in crude oil considerably deteriorate the quality characteristics of petroleum products, decreasing the stability of automobile gasolines and their susceptibility to additives, increasing the carbon deposition, enhancing the corrosion activity, and shortening the operation life of catalysts, pipelines, and process equipment at oil refineries. The possibilities of the hydrotreating technology have been virtually exhausted, and the reduction of the sulfur content of petroleum products to 0.001 wt % and lower levels by this method is economically unfeasible. Therefore, it is topical to develop new comprehensive, economically efficient, and highly productive processes for reducing the total sulfur content (to 0.001 wt % inclusive) of petroleum processing products and in the step of crude oil pretreatment without using hydrogen.

Various methods for deep desulfurization of hydrocarbon raw materials are discussed in detail in numerous papers. These papers have been reflected in part in reviews published mainly before 2008 [1–7].

Here we analyze papers published in the past decades on various methods, including oxidative desulfurization, for treatment of crude oil, petroleum fractions, and some other hydrocarbon mixtures containing sulfur compounds without using hydrogen.

OXIDATIVE DESULFURIZATION OF MODEL AND REAL HYDROCARBON MIXTURES WITH PEROXIDES

Procedures for removing sulfur compounds from hydrocarbon raw materials without using hydrogen can be considered as an alternative to hydrotreating. Among these procedures, oxidative desulfurization using various types of oxidants seems the most promising. In the course of oxidative desulfurization with hydrogen peroxide, sulfur-containing compounds are oxidized first to sulfoxides and then to sulfones. This method is simple and allows reaching very low levels of sulfur content of conventional crude oil [8], tight oil [9], and petroleum products with the removal of benzothiophene and dibenzothiophene derivatives exhibiting low chemical activity under the hydrotreating conditions [9–12]. The oxidized sulfur-containing compounds can be subsequently separated from the petroleum products by extraction from oxidized petroleum fractions with immiscible polar solvents or by adsorption.

Initially, oxidative desulfurization was performed using nitrogen dioxide (NO_2) as an oxidant and methanol as a solvent. Later numerous other solvents were studied in the course of development of this procedure.

Among all the oxidants, hydrogen peroxide proved to be the most suitable for converting sulfides to sulfoxides and sulfones, because it has the highest content of available oxygen (47.1%). The other advantages of hydrogen peroxide are relatively low cost, environmental safety, and commercial availability [13, 14].

It is most appropriate to perform liquid-phase oxidative desulfurization using hydrogen peroxide in a two-phase system allowing the use of dilute hydrogen peroxide solutions, easy separation of oxidation products from the main hydrocarbon fraction, and repeated use without regeneration of transition metal compounds added to enhance the oxidizing activity of hydrogen peroxide [15–19]. The main problem in using hydrogen peroxide as an oxidant in this case is low oxidation rate due to hindered mass transfer in the two-phase oxidation process and the subsequent power-consuming phase separation [20]. Carbonyl compounds are effective additives to hydrogen peroxide, as they significantly accelerate oxidation of sulfur organic compounds and increase the degree of desulfurization of oil fractions [21, 22]. Combination of hydrogen peroxide with complexes of various metals [23–29], as well as the use of an exogenic catalyst and a water-soluble acid [30, 31], ensures high degrees of oxidation of sulfur organic compounds of petroleum fractions. The oxidized sulfur-containing compounds can be extracted from petroleum products with polar solvents immiscible with the hydrocarbon fraction; then, the oxidized compounds and polar solvent are separated from the petroleum products by phase separation by settling or centrifugation. Sulfones are extracted with polar solvents such as acetonitrile, DMF, methanol, furfural, and DMSO under mild conditions with easy implementation and low operation cost. However, these solvents are volatile, harmful for the environment and humans, and insufficiently effective [32, 33]. Oxidation is performed by the reaction of the oxidant with the petroleum fraction under the conditions chosen so as to ensure the reaction cessation before the oxidants start to react with the other petroleum components, less reactive than the sulfur organic compounds [33].

An advantage of the process is that the oxidation system can be regenerated and reused. The efficiency of oxidative desulfurization of petroleum products with hydrogen peroxide decreases in the order light gas oil > commercial liquid fuel > clear cyclic fuel. The presence of olefins in catalytic cracking naphtha inhibits the desulfurization because of the occurrence of side oxidation of unsaturated compounds [12].

Vanadium pentoxide, sodium molybdate and tungstate, peroxotungstic and peroxomolybdic complexes, etc., are used as oxidative desulfurization catalysts, and lower carboxylic acids are used as cocatalysts [34, 35]. The use of the majority of these compounds, especially molybdenum derivatives, as catalysts is possible under homogeneous and heterogeneous conditions.

For example, a molybdenum-containing catalyst supported on Al_2O_3 exhibits higher catalytic activity in oxidation of sulfur compounds compared to the catalyst supported on TiO_2 or SiO_2 [36]. Nevertheless, the molybdenum catalyst is prone to leaching in the reaction medium in which the catalyst is not quite stable, and the active form of the catalytic system is the dissolved molybdenum compound. The degree of oxidation of each sulfur-containing compound increased with an increase in the O/S molar ratio. Wang et al. [36] believe that the oxidation of sulfur-containing compounds can be considered as a first-order reaction with the surface activation energy of $28 \pm 1 \text{ kJ mol}^{-1}$.

Polyaromatic sulfur-containing compounds such as dibenzothiophenes, naphthothiophenes, etc., appear to be more reactive in oxidative desulfurization than thiophenes and benzothiophenes [37, 38]. In polyoxometalate-catalyzed oxidation of sulfur-containing compounds, the reaction rate is controlled by the mass transfer through the interface of the aqueous and oil phases. In such cases, a phase-transfer catalyst is usually added to the system.

The performance of hydrogen peroxide as an oxidant was demonstrated in the presence of a heterogeneous catalyst, 15% $\text{MoO}_3\text{--WO}_3/\text{Al}_2\text{O}_3$, which ensured at 338 K up to 99.2% removal of thiophene derivatives from a model mixture [39]. According to [40], the heterogeneous catalyst $(\text{C}_4)_3\text{PMo}_{12}\text{O}_{40}/\text{SiO}_2$ efficiently catalyzes oxidation of benzothiophene, dibenzothiophene, and 4,6-dimethyldibenzothiophene with hydrogen peroxide under mild conditions. Another example of using a heterogeneous catalyst was reported

by Yashnik et al. [41]: CuZnAl formulations remove up to 40–45% of sulfur from a model mixture of toluene and dibenzothiophene. Sulfur is partially removed in the form of SO₂ and partially adsorbed on the catalyst surface.

Complete oxidation of dibenzothiophene with hydrogen peroxide was reached at 60°C, O/S molar ratio of 3.0, and thermal equilibrium in 100 min. The reactivity of the tested sulfur-containing compounds in oxidation decreased in the order dibenzothiophene > 4,6-dimethyldibenzothiophene > benzothiophene. Water and (C₄)₃PMo₁₂O₄₀/SiO₂ were readily separated from the hydrocarbon fraction by centrifugation; addition of quinoline and carbazole positively influenced the oxidation process, because these additives inhibit the thermal decomposition of hydrogen peroxide. Among other oxidation systems based on hydrogen peroxide, systems with crown ethers [42] and their complexes with amino acids [43] should be noted; these systems allowed oxidation not only of methyl phenyl sulfide, but also of weakly active benzothiophene and dibenzothiophene. In studies of oxidative desulfurization, various catalytic oxidation systems were suggested (H₂O₂/organic acids, H₂O₂/heteropoly acids, H₂O₂/MoO_x, H₂O₂/Ti-zeolite, systems based on *tert*-butyl hydroperoxide), and the mechanisms of their action were discussed [44–46]. In contrast to H₂O₂, *tert*-butyl hydroperoxide is fully soluble in crude oil, which eliminates the need for working with two-phase systems [45]. Quaternary ammonium cations and phosphotungstate ions also form an effective system for oxidative desulfurization of diesel fuel. The amphiphilic catalyst with the corresponding quaternary ammonium cation can form metastable emulsion drops in a diesel fuel with an aqueous H₂O₂ solution; in this case, the size and type of the quaternary ammonium cation play an important role in formation of metastable emulsion drops [44]. Al-Shahrani et al. [47] rationalized the detailed mechanism of the action of a homogeneous two-phase oxidative desulfurization system without using a phase-transfer catalyst: The formation of the two-phase system starts immediately on mixing of the catalyst with hydrogen peroxide and petroleum products in acetic acid.

Zhu et al. [48] suggested a general mechanism of catalytic oxidative desulfurization in four steps: (1) active peroxy complexes [Mo(O₂)] are formed by the reaction of [Mo(O)] when the ionic liquid based on polyoxometalate reacts with excess H₂O₂; (2) oxygen

transfer from active [(Mo(O₂))] to sulfide leads to the formation of the transition state; (3) oxygen is completely transferred to the sulfide molecule with the formation of sulfoxide and [Mo(O)]; (4) [(Mo(O₂))] participates in oxidative desulfurization with the formation of sulfone and regeneration of [Mo(O)].

Chen et al. [49] suggested a dibenzothiophene oxidation scheme involving the use of the ionic liquid [C₁₆mim][PyW] as a catalyst. According to the mechanism that they suggested, the formation of a hydrogen bond between the imidazolium cation and sulfur atom of the dibenzothiophene molecule plays an important role in enhancement of the desulfurization efficiency. Heterogeneous catalysts in the form of imidazole ionic liquids containing phosphomolybdic and phosphotungstic acid anions, immobilized on mineral supports, were suggested for oxidation of thiophene derivatives. Along with thiophene oxidation, the catalysts are active in desulfurization of straight-run diesel fraction and of synthetic petroleum obtained from oil shale [50]. The H₂O₂ concentration also significantly influences the desulfurization efficiency: The efficiency of oxidation of sulfur-containing compounds tends to increase with an increase in the molar ratio of the oxidant to sulfur-containing compound (O/S) [51].

Chen et al. [52] experimentally determined the influence of the O/S molar ratio on oxidation of sulfur-containing compounds in the presence of [C₄mim]Cl/3ZnCl₂. The oxidation efficiency increased from 18.6% at the O/S molar ratio of 2 to the maximal value of 99.9% at the O/S molar ratio of 8. However, with a further increase in the O/S molar ratio, the oxidation efficiency decreased (to 49.3% at the O/S molar ratio of 9). This fact allows a conclusion that the stoichiometric amount of H₂O₂ is insufficient for oxidation of the whole amount of dibenzothiophene because of partial decomposition of H₂O₂ in the course of oxidative desulfurization; therefore, certain excess of H₂O₂ is required to ensure complete oxidation of dibenzothiophene [53, 54]. However, too large excess of H₂O₂ negatively influences the removal of dibenzothiophene from crude oil [55]. According to [53], the degree of desulfurization of a model mixture was 76.3% when using 30% H₂O₂ and reached 97.9% when using 7.5% H₂O₂. Oxidation of sulfur-containing compounds with hydrogen peroxide is efficient in the presence of acetic acid and Ti-containing catalyst in the temperature interval 20–90°C. Then, the solvent and oxidation products are removed from

the hydrocarbon fraction by distillation and extraction [56, 57]. Various alkyl hydroperoxides in the presence of heterogeneous catalysts containing molybdenum, titanium, tungsten, and rhenium compounds are also used for oxidation of sulfur-containing compounds of crude oil and petroleum fractions. The activity of peroxides in oxidative desulfurization decreases in the order cyclohexanone peroxide > *tert*-amyl hydroperoxide > *tert*-butyl hydroperoxide [29, 58–61].

OXIDATIVE DESULFURIZATION USING OXYGEN

Molecular oxygen is widely used as an oxidant for conversion of sulfur organic compounds [62, 63]. Its use is efficient when combining the steps of catalytic oxidation and adsorption on the surface of an adsorbent (based on carbon-containing materials). The potential advantage of this approach is the use of molecular oxygen or air, i.e., of readily available and cheap reagents suitable for use in desulfurization. The process does not involve the use of peroxides and aqueous solutions; hence, it does not require the use of a crude oil–aqueous solution two-phase system, which considerably simplifies the process and reduces the fuel loss in phase separation of the liquid–liquid system. Although oxygen is undoubtedly an economically advantageous oxidant, it exhibits low activity, because its ground state is a triplet ($^3\text{O}_2$) of low energy. Various metal-containing catalysts such as V–Mo, Mn–Co, Co–Mo, Fe, Pd, Te, and Mo were used for oxygen activation in thermocatalytic oxidative desulfurization of liquid fuels [64–68]. The necessary condition for these reactions is that they should be performed with pure oxygen and/or at high temperatures or for a long time.

A procedure for oxidative desulfurization of crude oil under the action of oxygen is described in patents [69–71]. The catalysts used are phthalocyanines containing Co, Fe, Mn, or Ni, applied onto activated carbon or a polymer support based on polyethylene or polypropylene. The process is performed at room temperature with up to 100% conversion.

Ismagilov et al. [72] described a gas-phase oxidative process for desulfurization of diesel fuel on a heterogeneous catalyst at 300–400°C with a model mixture of thiophene, DBT, and 4,6-DMDBT in octane or isooctane as example. The process followed by hydrotreating ensures highly efficient desulfurization of diesel fuel.

Photocatalytic process with oxygen as oxidant is an efficient method of desulfurization without hydrogen. Such catalysts as CuW/TiO₂–GrO (graphene oxide), Pt–RuO₂/BiVO₄, and Pt–RuO₂/TiO₂ were suggested for this purpose [73]. However, this procedure is of limited use because of complex implementation and high cost.

Major attention is paid today to photocatalytic methods that do not require the use of metals [74]. High degree of desulfurization (80%) under the action of oxygen was reached using CuO/ZnO/Al₂O₃ mixed catalysts modified with boron and molybdenum [75]. Pysh'yev [76] reported data on noncatalytic desulfurization of fuel without action of light. The process was performed with air as oxidant at a temperature of approximately 200°C and a pressure of 30 bar. 70% conversion of sulfur-containing compounds into the corresponding sulfoxides and sulfones was reached. The reaction mechanism was not discussed in detail.

Recently there has been steady interest in polyoxometalates as catalysts of liquid-phase oxidation with oxygen or air [77]. For example, high performance of phosphomolybdate heteropoly anion as a catalyst in oxidative desulfurization of the diesel fraction with oxygen was demonstrated in [78]. Ding and Wang [79] have shown that polyoxometalate metal-organic structures can catalyze oxidation of dibenzothiophene with oxygen with 90% yield of dibenzothiophene sulfone at 90°C, reaction time of 240 min, and atmospheric pressure.

OZONE AS AN OXIDANT IN OXIDATIVE DESULFURIZATION

Ozone also shows promise as an oxidant for oxidative desulfurization. Its advantages are low cost and possibility of generation directly on the site [28, 80, 81]. Direct ozonation of fuels involves formation of dangerously explosive mixtures. Therefore, it seems appropriate to exclude direct contact of ozone with the fuel by using salts of various transition metals as catalysts of fuel ozonation. This allows not only the oxidizing power of ozone to be improved, but also the contact of ozone with the hydrocarbon medium to be avoided [82]. The use of transition metal salts improves the performance of ozone in oxidation of some organic compounds owing to additional generation of free radicals from ozone [82]. Oxidation of sulfur organic compounds does not occur when using as catalysts

transition metal salts without adding organic ligands. This is caused by the fact that the generated hydroxyl radicals are not stabilized in such systems and undergo decay before contact with sulfur organic compounds. Addition of an organic ligand, sodium gluconate or ethylenediaminetetraacetate (EDTA), to an aqueous solution of a metal salt sharply enhances the oxidizing activity of the system, and the total sulfur content of the fuel is considerably decreased [82].

For virtually all the metal compounds, sodium gluconate is preferable as ligand, because EDTA forms more stable complexes owing to strong chelating effect of four carboxy groups, which makes the metal ion less accessible to the reaction with ozone molecules. The catalysts based on copper, cobalt, and manganese salts show the highest performance in desulfurization, which agrees with published data on enhancement of the oxidizing power of ozone in the presence of these metal ions [82].

As the metal concentration in the solution is increased, the degree of removal of sulfur compounds varies insignificantly. Although an increase in the metal concentration leads to an increase in the concentration of the generated hydroxyl radicals, only a part of them have time to react with sulfur-containing compounds of the fuel before decay [82].

The use of dielectric barrier discharge (DBD) plasma, which is formed in a strong electric field with low energy and high efficiency, is considered as a novel and promising technology of desulfurization with ozone [83]. DBD plasma is widely used in modifications of heterogeneous catalysts [84], in organic synthesis [85], in treatment of exhaust gases and wastewaters [86], and in other fields. Ma et al. [87] described a system for oxidative desulfurization using as an oxidant ozone generated in a DBD reactor with a wire cylinder. The system ensured oxidation of benzothiophene, dibenzothiophene, and 4,6-dimethyldibenzothiophene to the corresponding sulfones and/or sulfoxides. 70% removal of sulfur-containing compounds was reached in 10 min of oxidation, and 99.9% removal, in 30 min. Thus, it can be assumed that ozone as an oxidant plays the major role in desulfurization. A system for oxidative desulfurization, including both oxidation with ozone and extraction of oxidation products of sulfur compounds with an ionic liquid, was later suggested on the basis of this result [87]. The efficiency of radiation-thermal cracking and oxidation of petroleum products increases

when using synergistic action of ozone-containing mixtures and ionizing radiation [88]. According to [89], it is possible to selectively ozonize heteroatomic compounds containing sulfur, nitrogen, and oxygen, present also in resins and asphaltenes, without affecting the petroleum hydrocarbons.

ADSORPTION IN OXIDATIVE DESULFURIZATION PROCESSES

Oxidative desulfurization of hydrocarbon fuel is intensified when the oxidation is followed by the adsorption of oxidation products on a solid adsorbent. Adsorption on solid supports, requiring no additional chemicals, is an efficient method for removing sulfones from petroleum fractions [90]. The adsorption is preferable over the solvent extraction, because it is environmentally cleaner and allows more complete removal of sulfur compounds from the reaction medium [91, 92]. According to [92], arenes and olefins inhibit the adsorption of sulfur compounds. Thiophene is adsorbed more weakly than tetrahydrothiophene and 4,6-dimethyldibenzothiophene. Combination of the peroxide oxidation of sulfur compounds in petroleum fractions in the presence of heterogeneous supports, followed by adsorption removal of oxidation products, was also described [93, 94]. Solid acid catalysts and/or activated carbon with supported transition metal oxide were used as heterogeneous catalysts. The following compounds are suggested as acid catalysts: zirconium sulfate, aluminum sulfate, sulfated tin oxide, iron oxide, zirconium molybdate, and tin oxide molybdate [93].

The efficiency of oxidative desulfurization with molecular oxygen in the presence of a heterogeneous catalyst, followed by adsorption on activated carbon under mild conditions (25°C), was also demonstrated in [95]. According to [92], the adsorption ensured complete removal of sulfones, whereas solvent extraction led to a decrease in the sulfur content of the diesel fuel from 1430 to only 216 ppm. Etemadi and Yen [96] believe that the consumption of the adsorbent for the adsorption is 33 times lower than the consumption of the solvent used for extracting sulfones.

Various adsorbents were used in the process: modified chitosan [93–95], granulated activated carbon [94, 97], modified activated carbon [94], and, for adsorption of sulfones, aluminum oxide [94]. Nevertheless, the

processes using these adsorbents are expensive, involve complex procedures for adsorbent pretreatment, and require additional expenditures.

Metal halides and oxides (PdCl_2 and Cu_2O), supported on SBA-15 and MCM-41, also showed high performance in desulfurization of jet fuel [98]. Cu_2O as adsorbent showed higher performance when supported on MCM-41, compared to SBA-15 support; also, it can be regenerated by heating in air and reused, which is an advantage [98]. Mineral clays as adsorbents are widely used in oil industry for various separation and adsorption processes, e.g., for removal of undesirable color from lubricating oil, separation of different classes of hydrocarbons, and removal of sulfur compounds from petroleum products [99]. These adsorbents are cheap, mechanically strong, and chemically stable [99, 100]. By now [101], data have been obtained on the desulfurization mechanism with various mineral clay adsorbents used for removing sulfones, e.g., benzothiophene sulfone.

Metal-organic framework (MOF) systems show promise for enhancing the efficiency of desulfurization without hydrogen. These systems are highly ordered three-dimensional polymers containing coordination compounds formed by metal cations with organic "linker" units [102]. Metal-organic frameworks are porous organo-inorganic hybrid nanomaterials with the specific surface area reaching $3000\text{--}5000\text{ m}^2\text{ g}^{-1}$ [103]. MOFs are of much interest for chemistry [104] owing to the following characteristics: (1) well-defined nanostructure; (2) very high total surface area, up to $5000\text{ m}^2\text{ g}^{-1}$; (3) small inaccessible volume; (4) presence of metal cations that can act as adsorption or catalytic sites; (5) moderate to high resistance to temperature, oxygen, and water. MOFs are subdivided into microporous, mesoporous, and macroporous. Mesoporous MOFs have the void size in the interval $2\text{--}50\text{ nm}$, which is comparable to, or even larger than the molecular size of typical organic compounds except polymers [104].

Adsorption and desorption of aromatic and heterocyclic compounds on mesoporous MOFs plays an important role in heterogeneous catalysis [105], in storage of gases, and in adsorption of volatile organic compounds [106]. In another paper [107] dealing with catalysis using MOFs, much attention is paid to synthesis, activation, and modification of the surface of such systems for separation of gaseous substances. Depending on the li-

gand structure and lattice dimensionality, open channels and pores with a size of up to several nanometers can be formed in metal-organic frameworks [108]. Various nanoparticles improving the adsorption can be deposited in the pores.

MOFs show promise for gas storage and separation, for water treatment, and for purification of fuels [109, 110]. Examples of using metal-organic frameworks for removing sulfur compounds from hydrocarbon mixtures, including fuels, have been reported [111]. For example, the use of Co-containing metal-organic frameworks $[\text{Co}_6(\text{oba})_6(\text{CH}_3\text{O})_4(\text{O})_2]_n \cdot 3\text{DMF}$ (TMU-11) allows the adsorption capacity for dibenzothiophene to be increased to 825 mg g^{-1} [112]. The $\pi\text{--}\pi$ interaction between the adsorbate and aromatic structure of the linker favors reaching high adsorption capacity [113], but the major contribution is made by the interaction with the coordination-unsaturated cobalt ions.

Copper-containing metal-organic framework MOF-199 as a nanocomposite with activated carbon also exhibits high performance in removal of sulfur compounds (H_2S , CH_3SCH_3) [114]. The capacities found for the composite are 8.46 and 8.53% for H_2S and CH_3SCH_3 , respectively; these values are 40–50% higher than the capacity of MOF-199. The systems Ga-soc-MOF and RE-fcu-MOFs systems, containing as additional functional groups fragments of substituted benzoic acid and 1,9-naphthalenedicarboxylic acid, and Y-fum-fcu-MOF (fum = fumaric acid) have also been reported; there are active in hydrogen sulfide adsorption [115–118].

Khan et al. [119] used for removing thiophene compounds from a hydrocarbon mixture systems based on metal-organic frameworks ZIF-8 and MIL-100 (Fe) with the ionic liquids and heteropoly acids introduced into the pores. The adsorption capacity of such nanocomposites appeared to be 1.5–2.5 times higher than that of the initial ZIF-8 and MIL-100 (Fe). Nickel nanoparticles (2 nm) supported on metal-organic frameworks MIL-101 (Cr) are also capable of adsorbing large amounts of thiophenes [120]. Introduction of copper chloride into the pores of the framework [121], as well as introduction of copper or cerium oxide particles [122], considerably increases the capacity for thiophenes.

Theoretical studies of the adsorption of sulfur compounds on metal-organic frameworks containing

coordination-unsaturated metal ions (Zn, Cu, Fe) have shown that the major factor determining the interaction and adsorption strength is the presence of strong Lewis acid sites [123]. Metal-organic frameworks were shown to surpass Y-type zeolites in the ability to take up sulfur compounds [124]. Catalytic properties of metal-organic frameworks UIO-66 (Zr) were also demonstrated by the example of oxidative desulfurization of a model mixture containing dibenzothiophene; its conversion reached 100% [125].

Carbon materials (e.g., graphene and carbon nanotubes) are an excellent alternative to metal-containing catalysts in various fields of catalysis [126]. Graphene as a promising metal-free catalyst attracts much attention in desulfurization of crude oil and petroleum products owing to its high specific surface area and fine structure of the layers. In particular, graphene contains aromatic (sp^2) and aliphatic (sp^3) domains, which readily form complexes with aromatic sulfur compounds and form active sites owing to the presence of oxygen-containing functional groups [127]. Among graphene applications, photocatalytic oxidative desulfurization has attracted much attention recently [128]. In this process, graphene oxide containing, e.g., a bismuth compound BiOBr [129] was used for photocatalytic desulfurization of a model fuel, a solution of dibenzothiophene in cyclohexane. Sun et al. [128] reached virtually 100% removal of dibenzothiophene from a model mixture in 2 h at a moderate temperature (30°C) with photochemical activation using a 150-W ketene lamp.

Another application of graphene oxide was reported by Zhang and Wang [130]. In the oxidation-adsorption process, they used along with graphene oxide modified nitric acid and activated carbon. The octanal-air system was used as an oxidant. The results of that study demonstrate high efficiency of the desulfurization using graphene oxide and activated carbon as adsorbents of oxidation products formed from dibenzothiophene derivatives present in the hydrocarbon medium. Zhang et al. [131] synthesized for the first time a catalyst with renewable function by reduction of graphene oxide using poly(1-vinyl-3-methylimidazolium bromide). Such modified ionic liquid not only served as a linker between the catalyst anion and nonpolar graphene, but also created the required dispersity of poly[BiEtIm] $[\text{PW}_{12}\text{O}_{40}]$ -GrO in the ionic liquid, ensuring the required exposure time of the immobilized catalyst surface in the

course of desulfurization. The degree of sulfur removal from a model mixture using this catalyst reaches 98% at eightfold repetition of the catalytic cycle.

High degree of catalytic oxidation of a model mixture containing dibenzothiophene and 4,6-dimethylbenzothiophene was reached with a heterogeneous catalyst containing phosphomolybdic acid $\text{H}_3\text{PMoO}_{12}\text{O}_{40}$ supported on graphene oxide [132]. Virtually 100% desulfurization was reached in 30 min at 50°C with sixfold use of the catalyst without appreciable changes in its performance.

Abdi et al. [133] used acetic acid modified graphene oxide as an oxidant and an adsorbent in oxidative desulfurization of a model mixture with the initial sulfur content of 1000 ppm under ultrasonic treatment. The sulfur content was decreased to less than 50 ppm in 300 min, which demonstrates high potential of the system in which the catalyst is simultaneously an adsorbent taking up oxidation products of sulfur compounds.

EXTRACTION IN OXIDATIVE DESULFURIZATION PROCESSES

Oxidative desulfurization using extraction attracts increasing attention because of relatively simple implementation. Numerous organic solvents, such as acetone, dimethylformamide, ethanol, acetonitrile, etc., are used for extraction of sulfur compounds from petroleum fractions. Extractive desulfurization processes using polar solvents in combination with oxidation have been described in sufficient detail in reviews [134–137]. The extraction does not alter the chemical structure of compounds in petroleum products and thus only slightly influences their quality [135]. Ethylene glycol oligomers [138] and choline chloride derivatives as eutectic solvents [139], combining proton acceptors and donors, were used for extraction of oxidation products of sulfur organic compounds from diesel fuel. The amount of the eutectic solvents required to remove the same amount of dibenzothiophene oxidation products is 3 times lower than the required amount of common polar extractants.

Some organic solvents can influence the inflammability and volatility of petroleum products [137]. In oxidative desulfurization of vacuum gas oil with hydrogen peroxide in the presence of an acid catalyst, followed by extraction of the oxidation products with acetonitrile, the sulfur content of the product was decreased to

11% of the initial level. The degree of desulfurization of vacuum gas oil appeared to be higher than that of desulfurization of light fractions [140].

The use of similar technology for oxidative desulfurization of pyrolysis tar in the presence of formic acid [141] allowed the sulfur content of the fractions obtained from the oxidized pyrolysis tar to be decreased by 75%.

Some ionic liquids (ILs) were also tested as extractants of sulfur compounds. The advantages of ILs as applied to the desulfurization process are high thermal stability, nonvolatility, and hydrophobicity [142–150]. The use of an ionic liquid for selective extraction of sulfur compounds from petroleum products was reported for the first time in 2001 [151]. Since that time, numerous ionic liquids containing such anions as alkyl sulfates, thiocyanate, acetate, dialkyl phosphate, or trifluoromethanesulfonate and such cations as pyridinium, imidazolium, or pyrrolidinium were used in desulfurization [143, 152–164], but the efficiency of desulfurization by extraction with ionic liquids is relatively low, less than 80% for the majority of ILs.

To enhance the IL performance, Gao et al. [165] synthesized pseudocarbonate with which the efficiency of the extractive desulfurization as high as 99% was reached, but they failed to regenerate and recycle the ionic liquid. Ko et al. [166], using Fe-containing ionic liquids with increased molar ratio of FeCl_3 to imidazolium chloride, equal to 2, reached almost 100% desulfurization, but recirculation of the ionic liquid was not studied. Many aromatic ionic liquids, including the most known ILs with the imidazolium cation, exhibit low selectivity in extraction of sulfur-containing heteroaromatic compounds relative to toluene because of strong similarity in the π - π interaction, and the content of alkylaromatic hydrocarbons in crude oil is up to 15%. Furthermore, these ionic liquids can partially dissolve in petroleum products, altering their composition and contaminating fuel oils. Magnetic ionic liquids exhibit not only excellent properties of common ionic liquids, but also good response to external magnetic field, which allows their easy separation from the reaction mixture and reuse [167]. For example, Zhu et al. [168] used magnetic ionic liquids based on pyridinium cation for oxidative desulfurization of diesel fuel with the subsequent restoration of their activity.

Extractive-oxidative desulfurization gives relatively good results when bifunctional ionic liquids with the an-

ion acting as oxidant, such as 1-octyl-3-methylimidazolium persulfate [169], or superbasic ionic liquids with Lewis acidity [170], e.g., protonated ionic liquid with the 1,5-diazabicyclo[4.3.0]non-3-ene cation and complex anion derived from ZnCl_2 [171], are used. Under optimum conditions of a one-step process, such ionic liquid allowed the sulfur content of a real diesel fuel to be decreased from 559.7 to 6.5 ppm, ensure 98.8% removal of total sulfur.

ULTRASONIC ACTION IN OXIDATIVE DESULFURIZATION

Ultrasonic oxidative desulfurization involves combined use of ultrasonic treatment, oxidant, and catalyst, followed by liquid–liquid extraction or adsorption to remove sulfur-containing compounds from the fuel [172]. Ultrasound can enhance the mass transfer and improve the oxidative desulfurization kinetics owing to the formation of voids in the liquid fuel [173]. The voids generated by ultrasonic irradiation increase the interfacial surface, which, in turn, accelerates the reaction. The formation of a fine emulsion by immiscible phases is considered as a physical effect, and the generation of radicals as a result of short collapse of cavitation bubbles, as a chemical effect of ultrasonic cavitation [174]. The efficiency of the ultrasonic treatment in oxidative desulfurization can be influenced by the nature of the hydrocarbon raw material and by the boiling range of the fraction [175]. The majority of studies on the use of ultrasound for oxidative desulfurization were performed with diesel fuel and model mixtures containing various sulfur compounds such as dibenzothiophene and its derivatives [156, 176–179].

One of the main limiting factors of these studies is long oxidation time. For example, according to [180], no less than 30 min is required to reach 87% degree of desulfurization. Therefore, today one of the main problems with using ultrasonic irradiation in combination with a simple and cheap oxidation system is reduction of the oxidation time. Dehkordi et al. [180] used a low-power (70 W) ultrasonic device for oxidation of model sulfur-containing compounds with the hydrogen peroxide–peracetic acid oxidation system. The total conversion of sulfur compounds in 1 h was 30%. The same device was used for oxidation of model sulfur-containing compounds under the action of the hydrogen peroxide–formic acid oxidation system and a

phase-transfer catalyst. The sulfur conversion was 47% in 1 h. In the suggested oxidation system, the phase-transfer catalyst promotes transport of the oxidant through the interface, which leads to an increase in the conversion of the sulfur-containing compound [181].

Optimization of the ultrasonic treatment in oxidative desulfurization is reached by improving the reactor design [182, 183], so as to ensure more pronounced synergistic effects and accelerate the mass transfer in the gas–liquid system. As demonstrated by the example of kerosene that had not been hydrotreated [182], the use of a surface-centered reactor with simultaneous action of ultrasound and UV irradiation ensured 91.7% degree of desulfurization and 48% degree of dearomatization. The latest advantages in the use of ultrasonic treatment for desulfurization are reflected in [184].

DESULFURIZATION USING SUPERCRITICAL WATER

Treatment with supercritical water (SCW) is also a potentially promising procedure for reducing the sulfur content, especially as applied to heavy petroleum fractions and crude oils [185]. SCW is a good solvent for activation of heteroatoms present in molecules of crude oil components, because C–O (as in ethers) and C–S (as in sulfides) bonds are cleaved in SCW more readily than under common conditions of “dry” pyrolysis [186]. In addition, SCW is a nonpolar solvent capable to dissolve organic compounds, including the majority of crude oil components. In some cases, the reaction rate and product distribution in reactions performed in SCW can be controlled by varying the conditions, e.g., the temperature, pressure, and concentrations of the reactants and catalyst [187]. SCW has the viscosity comparable to that of the gas, which accelerates the mass transfer relative to the liquid phase and allows some catalysts to preserve high activity for a long time [186, 187].

Different types of sulfur-containing compounds behave in the course of oxidation in SCW differently. Nonaromatic sulfur compounds, including sulfides and thiols, are cleaved in SCW, whereas aromatic sulfur compounds are more stable [187]. Because of the effect of sulfur on metal catalysts and oxidation of metal components in SCW, only a limited set of catalytic materials can be used in this process [188]. In addition, traditional materials for catalysts, such as silicon dioxide

and aluminum oxide, strongly degrade in supercritical water [189].

The catalyst stability in supercritical water was evaluated under the conditions of biomass gasification [188], when the problem of sulfur removal was not so significant as in petrochemical processes [189]. According to [189], oxides of Ce, Co, Fe, Mn, Ti, Mo, and Zn are usually used as catalysts for reactions performed in supercritical water. The use of supercritical water for improving the quality of crude oil leads to partial degradation of asphaltenes, to an increase in the content of light fractions, and to the suppression of coking [190, 191]. The use of supercritical methanol gives the same result, with a change in the content of heteroatoms in the final product, suggesting partial occurrence of desulfurization [192, 193]. Data on the use of SCW for sulfur removal, published in the past two decades, are discussed in detail in a review [194].

CONCLUSIONS

Summing up the above-discussed data, we can make the following conclusions. Several types of procedures for refining of hydrocarbon raw materials without hydrogen using oxidative desulfurization have been suggested:

- oxidative desulfurization on heterogeneous catalysts;
- oxidative desulfurization in the liquid phase (phase-transfer catalysis);
- desulfurization by ozonation;
- adsorption methods of oxidative desulfurization;
- extractive desulfurization, including processes using ionic liquids;
- ultrasonic desulfurization;
- desulfurization using supercritical water.

Each of these methods has certain advantages and drawbacks, and none of them has found commercial use comparable to that of hydrotreating. Oxidative desulfurization of various types of motor fuels can logically supplement large-tonnage hydrotreating and can potentially be used as a separate method for deep removal of sulfur. Taking into account the fact that efficient liquid-phase oxidative desulfurization requires large amounts of hydrogen peroxide and organic solvents for extraction of oxidation products, this method will hardly be used on a larger scale than the hydrotreating method.

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