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INVITED REVIEW PAPER

Selective oxidation of refractory sulfur compounds for the production of low sulfur transportation fuel

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Abstract−The current technologies for achieving low sulfur in diesel fuel are based on hydrotreating, which requires high temperature, high pressure and excessive supply of hydrogen. Oxidative desulfurization (ODS) is considered one of the promising new methods for super deep desulfurization, which could be carried out under very mild conditions (atmospheric pressure, <100 °C) without consumption of hydrogen. In this paper, development status of ODS process by major licensors are described as well as general concepts of ODS reaction. In addition, the ODS process has been categorized into single phasic and biphasic system according to the oxidants involved. Recent trends in both systems are reviewed in detail and future work is also proposed.

Key words: Oxidative Desulfurization, Refractory Sulfur Compounds, Selective Oxidation, Low Sulfur Fuel, Catalyst, Oxidant, Liquid Phase

INTRODUCTION

Although the demand for petroleum-based light oil products such as LPG, naphtha, gasoline, kerosene, and diesel are greatly increasing as base materials in the petrochemical and transportation industries, sour heavy crude oil of poor quality (high sulfur and nitrogen content, high TAN (total acid number)) are frequently found due to crude oil reserves, mining conditions and other factors [1]. It is well-known that a large variety of sulfur compounds (thiols, sulfides, disulfides and thiophenes) contained in liquid fuels generate sulfur oxides (mainly SO_2) and airborne particulate emissions during combustion, which has been recognized as a precursor of acid rain and air pollution [2]. The presence of sulfur also results in the corrosion of parts of combustion engines and refinery equipment because of the formation of oxyacids [3]. Furthermore, sulfur compounds in transportation fuels as a poison for the catalysts in catalytic converters. Therefore, stringent environmental regulations on the specifications of sulfur level in fuel oil have been imposed globally. By 2010, the sulfur content tolerated in many countries, both in gasoline and diesel, was less than 10 ppm [4,5]. Considering the growing trend of fuel consumption and exploiting petroleum resources, the remaining part of petroleum is more viscous and has a high sulfur content whose desulfurization will make the final desulfurized fuel product even more expensive [2,6]. As a consequence, the removal of sulfur of transportation fuel derived from heavy sour crude oil is extremely important in the petrochemical industry and development of deep desulfurization technology for the production of ultra-low sulfur fuel oil has become the target of worldwide researchers [1].

The most important and commercial route for desulfurization of light oil is the hydrodesulfurization (HDS) process. HDS process is operated under high temperatures (above 300 °C) and high hydrogen pressures ranging between 20-100 atm. over $CoMo/Al_2O_3$ or $NiMo/Al_2O_3$ as the catalysts [3,4,6,7]. One can refer to important review papers on this topic for more detailed information [5,6,8,9]. Even though the HDS is still considered as highly efficient for removing sulfur compounds in light oil and is preserving long lifetime of the catalyst (approximately two years of on-stream operation), extreme reaction conditions such as high temperature and high hydrogen pressure including the possibility of vaporization of light oil have to be considered for economic evaluation of process. The most considerable characteristic of HDS is that this common technology is limited to fulfilling the strict sulfur content regulations depending on the type of sulfur compounds to be converted. The HDS process can effectively remove aliphatic and acrylic sulfur-containing compounds (thiols, sulfides, and disulfides), while it is difficult to desulfurize refractory bulky polyaromatic sulfur compounds such as benzothiophene (BT), dibenzothiophene (DBT) and their alkyl derivatives, especially 4,6-dimethyldibenzothiophene (4,6-DMDBT) [10]. This limitation is attributed to not only steric hindrance of the bulky aromatic sulfur species restricting access to the catalyst active sites, but also the high electron density around the sulfur atom [11,12]. The removal of these refractory sulfur compounds using the deep HDS process is expensive and inevitably requires the application of extreme operating conditions: very low space velocities, high temperatures, high pressures and large hydrogen consumption, compared with conventional HDS of light oil [4,7,13]. Therefore, technology licensors and catalyst manufactures have continued to develop conventional HDS technology to reduce the capital and operating expense required, but not commercialized up to now.

There are alternatives to producing petroleum products with ultra-low sulfur content from the treatment of heavy sour feedstock containing large concentration of refractory sulfur compounds, in which they are developed as complementary (or secondary) desulfuriza-

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tion routes to conventional HDS technology [4,7,14]. For example, non-HDS technologies such as selective adsorption of sulfur, selective oxidation of sulfur, and biodesulfurization have been proposed. Song [5] reported that Pennsylvania State University has been exploring a new desulfurization process by selective adsorption for removing sulfur (PSU-SARS) at ambient temperature without using hydrogen or any other reactive gas [8]. In developing the PSU-SARS concept, the key consideration is to design the adsorbent materials to selectively interact with sulfur in the presence of large excess of aromatic compounds. More recently, Yang et al. [15,16] reported on adsorption separation of thiophenic sulfur compounds from aromatic compounds based on π-complexation using Cu- and Ag-exchanged Y zeolites. But, selective adsorption for removing sulfur has not successfully developed for liquid fuels due to the presence of many other compounds such as aromatics and polar species in refinery streams [5]. Biological method is another alternative option to remove sulfur from fossil fuel. Campos-Martin et al. [2] reported that some microorganisms can consume the sulfur in thiophenic compounds such as DBT and reduce the sulfur content in fuel. In this paper, two main pathways have been reported: ring-destructive (degradation) and sulfur-specific (desulfurization) pathways in terms of DBT utilization. To date, two ring-destructive pathways for metabolism of DBT have been recognized. They concluded that in order to make the biodesulfurization process competitive with deep HDS, a five-step process is needed: (i) production of active resting cells (biocatalysts) with a high specific activity; (ii) preparation of a biphasic system containing oil fraction, aqueous phase and biocatalyst; (iii) biodesulfurization of a wide range of organic sulfur compounds at a suitable rate; (iv) separation of desulfurized oil fraction, recovery of the biocatalyst and its return to the bioreactor; and (v) efficient wastewater treatment. Each step is affected by a number of factors [2]. However, selective adsorption and biodesulfurization methods are still not economically viable at a commercial scale [4,7]. Meanwhile, selective oxidative desulfurization (ODS) processes have been attracting much attention due to their progress to a state where nearing commercialization. Compared to deep HDS process, ODS process could be operated under very mild conditions (atmospheric pressure and low reaction temperatures) and provide much more advantage that does not use hydrogen because hydrogen balance is generally tightened in the refinery field. Furthermore, refractory organic sulfur compounds such as dibenzothiophene and 4,6-dimethyldibenzothiophene are easily removed by ODS process where high electron density on the sulfur atom renders aromatic organic sulfides more susceptible to the electrophilic attack of the oxidizing agent, resulting ultimately in the corresponding sulfones [12,17]. Therefore, integration of ODS with a conventional HDS is considered as a promising way to achieve an ultra-low level of sulfur in petroleum products [3,4,7,14]. In this paper, we focus on the recent

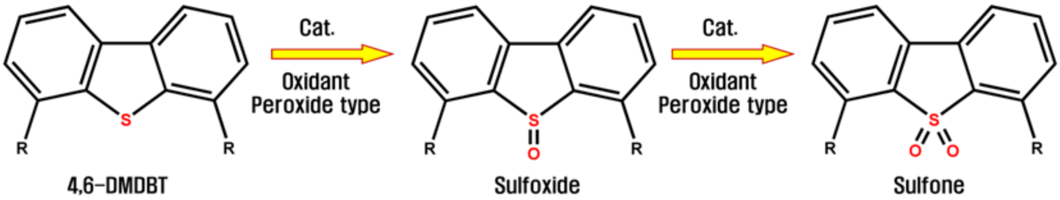
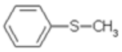
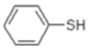
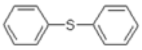
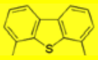
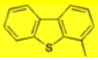
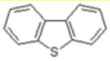
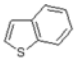
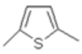
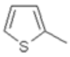
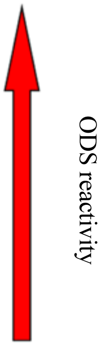


Fig. 1. 4,6-Dimethyldibenzothiophene oxidation chemistry.

Table 1. Electron densities on sulfur atom and rate constants [12]

Sulfur compound	Structure	Electron density	K (*l*/mol·min)
Methyl phenyl sulfiode		5.915	0.295
Thiophenol		5.902	0.270
Diphenyl sulfide		5.860	0.15600
4,6-DMDBT		5.760	0.07670
4-MDBT		5.759	0.06270
Dibenzothiophene		5.758	0.04600
1-Benzothiophene		5.739	0.00574
2,5-Dimethylthiophene		5.716	-
2-Methylthiophene		5.706	-
Thiophene		5.696	-



Oxidation: Hydrogen peroxide+formic acid
Extraction: DMF

advancements in the ODS process among the alternatives of the HDS process and some results obtained by the authors' laboratories will also be discussed.

GENERAL CONCEPTS OF ODS PROCESS

The ODS process generally consists of two consecutive steps, the first step of which is selective oxidation of non-polar organic sulfides into highly polar sulfones (see Fig. 1), followed by a second step of subsequent separation of the polar sulfone compounds by extraction with a polar solvent or by adsorption. The sulfur atoms have d orbital, which enables oxidation of organic sulfur species into sulfone and sulfoxide [1]. In addition, the ODS reactivity of sulfur compounds is increased with the increase of electron density of sulfur atoms. The reactivity of DBT (Dibenzothiophene) derivatives is influenced by the electron donation of substituted methyl groups, reversing the order of reactivity of HDS [12]. Electron density data of sulfur compounds are listed in Table 1.

The ODS process has been developed by a variety of major licensors since 1996 and five pilot plants have been operated in the world, while not being commercialized up to now. PetroStar developed the CED (conversion/extraction desulfurization) process in pilot plant scale of 5,000 bbl/day at the end of 2000, in which sulfur concentration of feedstock (4,200 ppm) was reduced to below 10 ppm [18]. In the first oxidation step, sulfur compounds were oxidized to sulfone by using peroxyacetic acid under 75-90 °C and atmospheric pressure within residence time of 30 min. Hydrogen peroxide consumption to make peroxyacetic acid corresponds to half of the total operating cost. After the oxidation step, sulfone separation was conducted through liquid/liquid extraction to raffinate fraction with lower sulfur amount and extract fraction with high sulfur concentration. Raffinate was treated with adsorbents such as clay, silica gel, and alumina to remove residual sulfur species. After the recovery of solvent, extract was converted to sulfate, sulfite and sulfonate products by chemical treatment or mixed with raffinate after biological treatment in order to improve the economics. However, this process contains several disadvantages, of which HCOOH as oxidation catalyst is hard to separate and residual acid in the product might make trouble in color and phase separation.

The ASR-2 process, which was developed by Unipure in 2001, is based on the oxidation catalyzed by hydrogen peroxide in the presence of formic acid or acetic acid [19]. In this process, the diesel feed of up to 500 ppm sulfur is reduced to 5 ppm sulfur content at 120 °C and atmospheric pressure. Used catalyst and sulfone containing liquid stream are transferred to a catalyst recovery unit to sulfone removal and catalyst regeneration. Oil stream is moved into the extraction unit using methanol and solid adsorbent to remove residual sulfone species. Similar to the CED process, ASR-2 also has the problem of separation of liquid catalyst.

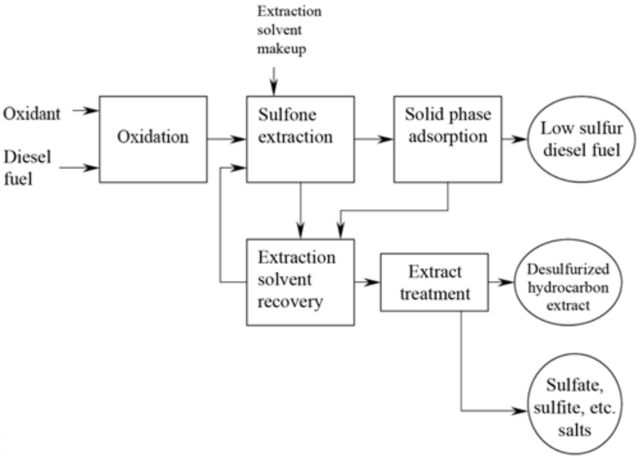


Fig. 2. Scheme of CED process [18].

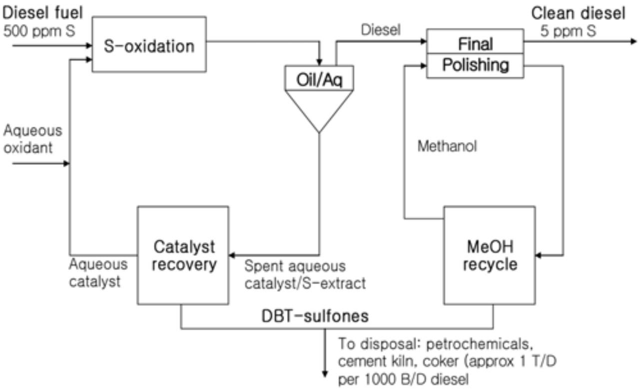


Fig. 3. Scheme of ASR-2 process [19].

SulphCo reported that oxidation efficiency was improved by applying ultrasound process (Sinclare), which is the core of SulphCo's reactor [20]. It generates tiny bubbles by cavitation in the range of 200 μm followed by sudden collapse. Through this process, violent micro mixing of different phases occurs and generates free radicals or excited oxygenates like hydroperoxide. The mixture of straight-run diesel and FCC LCO (light cycle oil) with the ratio of 7/3 was treated by Sinclare process and initial sulfur content of 3,000 ppm decreased to below 15 ppm of sulfur content and its yield was almost 100%. Ultrasonic oxidative desulfurization has high desulfurization efficiency, but still applied H_2O_2 as oxidant, and at the same time ultrasound device was used, which enhanced the cost and limited the scale of production [1].

Lyondell developed ODS process which was confirmed by the operation of pilot plant unit during 3,000 hours [21]. The fuel is oxidized with organic hydroperoxide in the presence of a heterogeneous oxidation catalyst (Ti/SiO_2) to form a sulfone product, followed by extraction of the sulfone by solid-liquid or liquid-liquid extraction. The fuel is then contacted with a decomposition catalyst to remove the residual organic hydroperoxide from the fuel. They found that the alcohol removal step prior to sulfone extraction resulted in greater adsorption capacity for the adsorbent.

The UOP/Eni oxidative desulfurization process consists of three process steps: an oxidant supply section, a sulfur reaction section, and finally a sulfone separation section [4,22]. This technology uses organic peroxide as an oxidant. The oxidant supply section can consist either of the handling equipment associated with purchase organic peroxide, or the peroxide can be generated internally via direct oxidation of a hydrocarbon with air. The use of an organic peroxide as the oxidant avoids the need to recycle corrosive organic acid catalysts that are needed when hydrogen peroxide is used. UOP/Eni has evaluated both extraction and adsorption separation, and concluded that the adsorption route is more cost-effective.

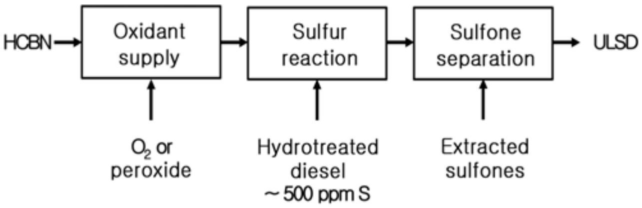


Fig. 4. UOP/Eni oxidative desulfurization process [4].

RECENT STUDIES OF ODS PROCESS

In the oxidation step, two types of oxidation systems are usually implemented, depending on the reaction conditions, that is, according to the type of oxidant and reaction phase [1,2,14]. The type of oxidant and catalyst is closely related to the reaction phase.

1. Biphasic ODS System

Oxidants such as hydrogen peroxide (H_2O_2) and organic carboxylic acids, soluble in polar solvents, are used to form a liquid biphasic system with the oil phase and the polar phase containing the oxidizing agents [10]. Nitric oxides and nitric acids were used for ODS reaction in initial studies, but were discarded due to their inevitable high amounts of residual products [23].

Afterward, the most well-known biphasic ODS process was developed by using organic peracids and hydrogen peroxide. The peracids, which are used for their powerful oxidation ability, are produced in situ by reaction of hydrogen peroxide and carboxylic acids due to their higher reactivity and corrosiveness. And hydrogen peroxide with a high amount of active oxygen (47 wt%) as an oxidizing agent is a commercial product and gives no pollutants [24]. After the earlier studies on the use of peracids in the oxidation of sulfur compounds [12,25], H_2O_2-organic acid systems have also been reported [26-30], but the applicability of these studies at an industrial level is restricted due to excessive consumption of oxidant and mass transfer limitations leading to very long reaction time.

To overcome these problems, addition of catalysts has been considered to provide additional oxidizing ability for ODS reaction. Transition metal salts have been used as a catalyst due to their high oxidation state with Lewis acid sites. Among the transition metal salts, tungsten salts are very active and selective in the oxidation of sulfur compounds with peracids [31,32]. Other transition metal salts such as Co [33,34] or Fe [35] are also used for ODS with peracids, which enable forming of reactive radicals having high oxidation capacity from peracids. Modified activated carbon with carboxylic groups was also used as a catalyst for ODS reaction with peracids [36-38].

In the H_2O_2 oxidation system, biphasic ODS reaction has been carried out using a variety of homogeneous metal catalysts: Co^{2+}, Sn^{2+} and Pd^{2+} [39], polyoxometalate [40-42], an iron containing tetraamidomacrocyclic ligand (TAML) catalyst, Fe-TAML® [43], sodium tungstate and sodium hydrogen sulfate [44], etc. Among them, polyoxometalates have long been studied for oxidation reactions, particularly, the polyoxometalate/hydrogen peroxide system for organic substrate oxidations due to their good transmission and storage capacity to electrons and protons, reactivity of lattice oxygen and high proton acidity [1,40]. A series of polyoxometalate/H_2O_2 systems were evaluated for dibenzothiophene oxidation. The H_2O_2 solutions of phosphotungstic acid and its salt were very active catalyst systems for the model compound oxidation, while their molybdenum counterpart systems were much less active. The H_2O_2 solu-

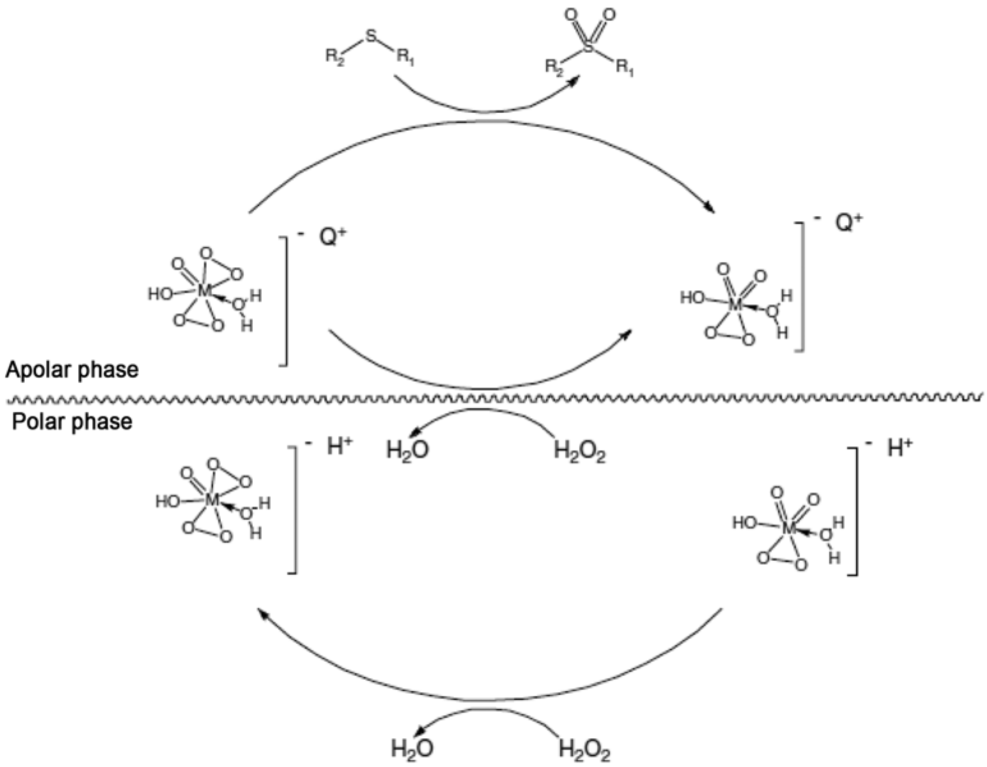


Fig. 5. Biphasic ODS reaction catalyzed by metallic peroxides [2].

tions of silicotungstic and silicomolybdic compounds were the least active catalyst systems for the reaction [41]. However, the surface of polyoxometalates is so small and easily lost in the ODS process that loaded-heteropolyoxometalate catalyst is considered to overcome these shortcomings [45].

When using peracids or hydrogen peroxide in the ODS process, these are not soluble in oil phase and form two immiscible liquid phases (an oil phase with sulfur compound and a polar phase with oxidant) in the reactor. For this reason, sulfur compounds are unable to fully access to oxidants. Therefore, phase transfer compounds have been significantly investigated [46-52]. The presence of the phase transfer agent facilitates the transfer of products and reagents at the polar-apolar interface, increasing mass transfer across the interface. Reaction mechanism of biphasic ODS reaction including phase transfer catalyst is proposed in Fig. 5 [2]. However, due to the insufficient mass transfer ability of above biphasic system, a special reactor design for the reaction homogenization, e.g., a continuous stirred-tank reactor (CSTR), microemulsion reactor, or microstructured reactor, has been studied to avoid the mass transfer limitation [23,53-55]. In addition, contamination of the oil by polar solvents such as water or alcohols as well as the need of large amounts of solvent may prevent industrial applications of the liquid biphasic system [1,14,56-58]. Compared to homogeneous catalysts, a variety of heterogeneous catalysts such as solid redox catalysts (Ti, V, W, Mo, Co/Mn, Ag, Au, Re) have been applied to the biphasic ODS system, which is recyclable to minimize pollution levels and provide higher atom utilization efficiency [2].

2. Single-phasic ODS System

The single liquid phase oxidation system can be operated by using organic hydroperoxides which are soluble in oil compared to biphasic ODS system using peracids or hydrogen peroxide as water-soluble oxidants. This single phase system exhibits more process-oriented characteristics from the following advantages: no emergence of oil emulsion as a result of the existence of water, a shorter time to mix organic peroxide with oil, enabling the application of a simple fixed bed system [1,2].

Tert-butyl hypochlorite was used as an oil-soluble organic oxidant for the oxidative removal of DBT at the beginning of single phase ODS system [59]. The results indicated that the conversion of DBT to DBT sulfone reached 90% at 50 °C under ambient pressure for both the flow system and batch system. The gamma alumina supported catalyst was necessary for this reaction system. The most widely used organic oxidant is *tert*-butyl hydroperoxide (TBHP). In the development of pilot-scale or commercial ODS process, UOP disclosed the continuous fixed-bed ODS system using *tert*-butyl hydroperoxide combined with adsorption for the separation of sulfone. They suggested the in-situ generation of the peroxide via direct oxidation of a hydrocarbon with air to overcome the drawbacks of high price and transportation problems of organic peroxide [22,60,61]. More recently, Lyondell also disclosed the fixed-bed system using *tert*-butyl hydroperoxide as a candidate of a pilot-scale process [62,63]. Zhou et al. reported that cyclohexanone peroxide (CYHPO) is more attractive as an oil soluble oxidant because it is comparatively cheap compared to other oil-soluble oxidants and large-scale industrial supply, although the conversion of DBT oxidation is still not enough to meet the need of deep desulfurization [64]. They also showed that the activity of alkyl peroxides decreases in the order of CYHPO>TAHP (*tert*-amyl hydroperoxide)>TBHP, reversing the order of the peroxy oxygen electronic density [65]. In the US patent 8283498 B2, diesel containing DBT may be oxidized using a heterogeneous titanium (IV) catalyst and organohydroperoxide, such as cumyl hydroperoxide (CHP) and ethylbenzene hydroperoxide (EBHP) as well as TBHP, which proves effective for the selective oxidation and removal of refractory sulfur compounds from diesel fuel [66].

The selective oxidation of the sulfur-containing compounds using organic hydroperoxides can be operated in the presence of transition metal-based catalysts (Mo, Ti, Fe, V, W, etc.), exhibiting high oxidation states with suitable Lewis acidity and redox properties [56,67]. Molybdenum catalysts such as heterogeneous Mo/Al_2O_3 have been intensively studied [13,17,68-70]. Wang et al. [17] reported that Mo/Al_2O_3 catalyst showed the optimum oxidation activity of DBT at around 16 wt% of Mo loading, and addition of Co and Ni onto the Mo/Al_2O_3 catalyst led to a significant decrease in ODS activity. The reactivity of sulfur compounds decreases in the order of DBT>4-MDBT>4,6-DMDBT>>BT, which is very different from the result of the biphasic oxidation [12]. It can be suggested that the oxidation reactivities of DBTs over Mo catalyst varied depending on two factors: the electron density of the sulfur atom in DBTs and the steric hindrance of methyl substitution when the sulfur in DBTs adsorbed on the surface of catalyst [17,69]. They also proposed a peroxidic oxidation mechanism of DBT on MoO_3 catalyst with *tert*-butyl hydroperoxide as shown in Fig. 6. The coordination of hydroperoxide to Mo-O is prompted by the polarization of $Mo^{\delta+}$-$O^{\delta-}$ bond when MoO_3 is dispersed on Al_2O_3, and electrophilicity of peroxy oxygen is prompted [17]. However, catalyst deactivation can occur due to metal leaching and the Mo tendency to be leached into the reaction medium in single phasic ODS reaction condition [56,71].

Chromium-containing catalysts have been investigated for the single phasic ODS reaction and selective oxidation of tetralin [72,73]. Among the transition metal substituted HMA and AlPO-5 catalysts, Cr-HMA showed higher activity than Co-HMA and Fe-HMA. However, the activity of chromium-containing catalyst is much lower than that of titanium-containing catalyst. Caero et al. [74] carried out oxidative desulfurization of synthetic diesel in the presence of V_2O_5/Al_2O_3 and V_2O_5/TiO_2 catalysts. They reported that V_2O_5/Al_2O_3 catalyst showed higher ODS activity than V_2O_5/TiO_2 catalyst, and nitrogen compounds retarded the oxidation reaction due to their preferential reactivity compared to that of DBTs.

Titanium-containing catalysts have been known to be the most effective catalysts for ODS both in biphasic and single liquid phase operating systems [7,56,67,75-80]. Kim et al. [10] described the characteristics of titanium-containing catalyst for ODS reaction that these preceding studies showed that the activity and lifetime of the ODS catalyst are influenced by several factors, including the nature of the coordination environment around the titanium center, struc-

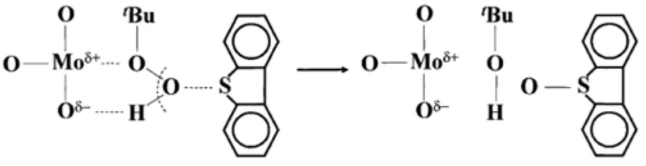


Fig. 6. Proposed peroxidic oxidation mechanism of DBT with tert-butyl hydroperoxide [17].

tural and surface properties of the material, type of oxidizing agent, reagent ratio, reaction temperature [56,75,81].

Microporous zeolitic TS-1 has been tested for this reaction because TS-1 is the commercial selective oxidation catalyst for epoxidation of propylene using TBHP as an organic oxidant. TS-1 is able to oxidize sulfur compounds, but its activity is not high enough to oxidize the refractory bulky sulfur compounds due to its medium pore structure [56,67], while thiophene, which is not easily removed by ODS reaction, could be oxidized over framework Ti species. Non-framework titanium in the catalyst is not the active site and a steric obstacle was also observed by using different crystal size of catalysts [80]. To overcome the steric hindrance of TS-1, mesoporous TS-1 with enhanced accessibility of bulky molecule to allow the active sites has been investigated [76,82]. Mesoporous TS-1 synthesized via a hybrid SiO_2-TiO_2 xerogel route combined with an organosilane additive showed higher than conventional TS-1 catalyst in single phasic ODS reaction [82]. Fang et al. [76] reported that mesoporous TS-1, with additional mesopore system formed by packing the TS-1 nanocrystals, was synthesized by nanocasting route using nanoporous carbon (CMK-3) as template. Its catalytic performance of mesoporous TS-1 in H_2O_2 oxidation of aromatic thiophene was improved compared with common TS-1 and is able to catalyze oxidation of bulky sulfur containing molecules such as DMDBT. Other zeolitic titanosilicate catalysts such as Ti-β [56,67], Ti-MOR [83], Ti-ITQ-7 [84], and Ti-MWW [75,85] have been studied. Among them, Ti-MWW has received attention because it has the unique sinusoidal 10 MR channels of the so-called within layers of MWW zeolite together with the open reaction spaces of 12 MR side cups and supercages than the tunnel type 10 MR channels of TS-1. Ti-MWW exhibited higher activity than Ti-MCM-41 showing low intrinsic activity due to its amorphous mesoporous walls and the reactivity of model sulfur compounds decreased in the order of DBT>4-MDBT>4,6-DMDBT>>BT [75]. Since mesostructured molecular sieves of MCM-41 type have been suggested as good support, mesoporous Ti-silica (Ti-MCM-41 [56,77], Ti-HMS [67, 79], Ti-SBA-15 [10,32]), and commercial amorphous titania-silica (TiO_2/SiO_2) [21] were previously tested as selective oxidation catalysts for ODS. Mesoporous Ti-silica (pore size>2 nm), was reported to exhibit higher catalytic activity and longer lifetime than microporous catalysts (pore size<2 nm) such as TS-1, in which organic sulfur compounds have restricted access to the active site due to the small zeolitic pore apertures. Chica et al. [56] reported that calcined Ti-MCM-41 was more active, did not leach Ti, and deactivated more slowly than MoO_x/Al_2O_3 catalyst for ODS reaction of model sulfur compounds. Jeong et al. [77] synthesized the titanium-containing MCM-41 like mesoporous silica catalysts (Ti-MMS) from fluorosilicon compounds (H_2SiF_6) and suggested that Ti-MMS with higher concentration of framework Ti species and significantly small cluster and primary particle size showed higher activity compared with Ti-MCM-41. Recently, our laboratory synthesized a series of mesostructured Ti-SBA-15 catalysts with the aging step conducted at different temperature (e.g., 35, 100, and 140 °C) in order to vary substantially the size of the mesopores and different Ti loading. Among them, catalytic results revealed that Ti-SBA-15 catalysts exhibiting the largest pore size (>7.3 nm) and high Ti content (>2.8 mol%) act as highly active catalysts for ODS reactions [10]. These results are in good agreement with the activity order of Ti/SiO_2 gel catalysts, showing good mechanical strength and thermal stability, in which pore size in the range of 7-10 nm showed the maximum ODS activity using TBHP as an oxidant.

The other most relevant parameters are the amount and nature of the Ti sites dispersed on the silica support. In particular, the presence of tetrahedrally coordinated Ti sites is critical, as the selective oxidation of the sulfur compounds proceeds through the initial addition of the peroxide (the source of oxygen) to the coordination-unsaturated metal center [10]. The higher catalytic activity of TS-1 and Ti-MCM-41 in selective oxidation reactions is probably a consequence of the formation of hydroperoxy species (Ti^{4+}-O-O-H) on their surface during the catalytic reaction. On the contrary, extra-framework Ti of ETS-4 and ETS-10 cannot form active titanium hydroperoxy species [77,86]. Conventional co-condensation or impregnation methods for the incorporation of Ti species into mesoporous silicates generally lead to generating small amounts of highly active tetrahedrally coordinated Ti^{4+} species on the surface while octahedrally coordinated anatase TiO_2 is formed in extra-framework of silicates. To overcome these problems, Capel-Sanchez et al. [87] employed various titanium precursors for the preparation of supported titanium catalysts, and their results showed that chemical grafting of titanium is produced by reaction between alkoxide precursor and surface OH groups, and samples prepared with titanium isoproproxide yield polymeric titanium species in tetrahedral coordination, which gives rise to a low-efficiency oxidation catalyst. However, when an antane is used (titanium (triethanolamiante)) isopropoxide), the isolated active titanium species is obtained due to the protective effect of the triethanolaminate. When this catalyst was used, the remaining sulfur concentration in the kerosene (1,219 ppm S) was below 240 ppm after 5 min, and below 10 ppm after 15 min [81]. Specifically designed Ti-SBA-15 catalysts were synthesized according to a post-grafting route based on the controlled insertion of titanium chelate species, as recently reported [88,89]. The synthesis of the Ti-SBA-15 catalysts is based on the use of a titanium alkoxide as the Ti source modified with acetylacetone (acac), which acts as a chelating agent in the post-grafting process (See Fig. 7). This specific synthesis method ensures high dispersion of Ti^{4+} sites in tetrahedral coordination placed on the mesopore surface, while enabling a facile tailoring of Ti loading and material porosity, result-

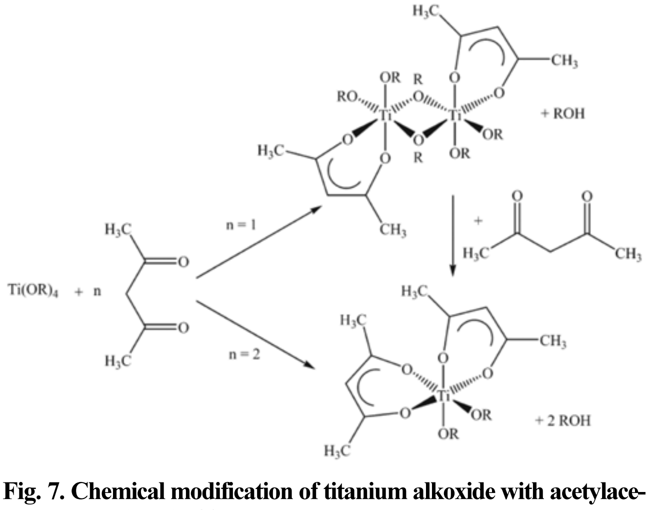


Fig. 7. Chemical modification of titanium alkoxide with acetylacetone (acac) [89].

ing in highly efficient removal of refractory sulfur compounds in a fixed-bed reactor with organic hydroperoxide [10].

Even with the impressive development of single phasic ODS catalyst and process, maintaining an extended lifetime under industrially relevant conditions is still difficult. Deactivation of ODS catalyst could be attributed to adsorption of nitrogen and sulfone compounds on the catalyst surface. Caero et al. [90] carried out ODS reaction of a synthetic diesel containing nitrogen compounds, and in the presence of nitrogen compounds the ODS activity decreased in the order: quinolone>indole>carbazole. The results show that DBT is displaced by quinolone, occupying the adsorption sites of catalyst. Nitrogen compound effect could be explained by strong adsorption of nitrogen compounds on catalytic sites. Furthermore, catalyst deactivation can occur due to adsorption of the highly polar sulfones produced in the reaction on the catalyst hydrophilic surface. In single phasic ODS reaction using TBHP as oxidant, sulfone compounds are present in the reaction mixture, and this species is responsible for the deactivation. However, in case of biphasic ODS system, sulfones are removed continuously from the liquid fuel by the polar solvent as is produced [81]. Hydrophilic surface characteristic has been modified by silylation of surface of titanium catalyst to increase the hydrophobicity of the surface [10,56,81]. Adsorption of highly polar sulfones on hydroxylated surfaces on the Ti-MCM-41 and Ti-SBA-15 catalysts is strongly suppressed by silylating the catalyst, generating a more hydrophobic surface and significantly increasing catalyst life [10,56]. Silylating reagents such as chlorosilanes, alkoxysilanes, and silylamines have found widespread application, and their reaction with surface silanol functionalities has been reported in detail [91-95]. Hexamethylenedisilazane (HMDS) is mostly used as silylating agent for epoxidation and ODS reaction. HMDS has organic silanes with three methyl groups (-Si-$(CH_3)_3$) while tetramethyldisilazane (TMDS) contains organic siliane with two methyl groups and one hydrogen (-Si-$(CH_3)_2$H). Therefore, TMDS affords the highest surface coverage, which makes this reagent superior to the commonly used standard silylation reagent HMDS. This higher silylation efficiency of TMDS might have important implications for the tuning of the catalytic properties of heterogeneously acting ODS catalysts. Sterically bulkier disilazane reagents such as tetraphenyldimethyldisilazane produce a surface morphology with a considerable number of uniformly distributed silanol sites left, which, however, are accessible for further modification reactions [96]. Our laboratory disclosed the effect of silylating agents (HMDS, TMDS, TMCS (trimethylchlorosilane) on ODS activity, indicating that TMDS is the best silylating agent for the activity and stability of Ti-acac-SBA-15 catalyst [97].

The effect of the amount of oxidant on the oxidation activity has been investigated because oxidant/sulfur ratio (O/S) is one of the critical factors for determining the potential of the ODS process for a commercial unit due to high price of oxidant. Two moles of oxidant are required to oxidize one mole of sulfur compound for stoichiometric oxidation reaction. Wang et al. [17] carried out the oxidation of simulated sulfur compounds over Mo/Al_2O_3 catalyst using *tert*-butyl hydroperoxide with different O/S ratios. ODS activity of each sulfur compound increased with the increasing O/S molar up to 3 and then leveled off beyond this value. This higher value may be attributed to the decrease in the concentration of oxidant due to its low thermostability at reaction temperature of 80 °C. Ishihara et al. [68] reported that oxidation activity of the sulfur compounds in the light gas oil (LGO) increased with the O/S molar ratio up to 15 and slightly decreased beyond this value, which was due to side reactions involving the oxidation of other major compounds of LGO, such as olefins and nitrogen compounds, which consume *tert*-butyl hydroperoxide. Similar behaviors of the effect of O/S ratio on ODS activity are also reported in other studies [32,69,77,98].

In spite of significant improvement in the design of ODS catalytic system, new insights into the role of the different structural and compositional parameters will be critical to design adequate and optimized catalysts and provide a deep understanding of the structure-reactivity relationship in this system.

FUTURE WORK

Oxidative desulfurization has proved to be a promising technology for the removal of refractory sulfur compounds which cannot be treated by the conventional hydrodesulfurization process. It can be operated under very mild reaction conditions and no consumption of expensive hydrogen, which can serve as a complementary option with conventional HDS. Even though there has been considerable progress recently in the development of the ODS process, a number of problems have not yet been solved to make the ODS process competitive with deep HDS.

This single phase ODS system exhibits more process-oriented characteristics, but organic peroxide as oxidant is too expensive and cannot be produced in refinery section for securing safety. So, some approaches should be considered for in-situ generation of organic peroxide from the feed mixtures containing appropriate benzylic carbon compounds. Clearly, it is highly desirable to oxidize sulfur compounds in fuels with oxygen or air, enabling avoiding the use of expensive organic oxidants or hydrogen peroxide. In addition, economic sulfone separation units (extraction or adsorption) are needed to commercialize the whole process. Most previous studies have mentioned that sulfone compounds can be easily separated by conventional extraction/adsorption method. Unfortunately, the operating and construction cost of a sulfone separation unit is much higher than that of an oxidation unit. Furthermore, it is very difficult to find an efficient and economic solvent combined with the generation of catalyst and adsorbent. In case of biphasic ODS system, intrinsic activity of the catalyst should be greatly improved at lower oxidant/S ratios as well as the development of reactor design to increase the mass transfer between polar and apolar phase.

Sulfone compounds generated through ODS process are actually low valuable products compared to feedstocks such as LCO (light cycle oil), HCN (heavy cracked naphtha), etc. Firstly, oxidized sulfur compounds can be returned into a mild hydrotreating unit because sulfone compounds are easily converted to S-free fuel, which is different from refractory sulfur compounds. Catalytic decomposition of sulfones has also been investigated by using basic catalysts like MgO and hydrotalcites. However, upgrading of sulfone compounds has to be greatly improved in the future.

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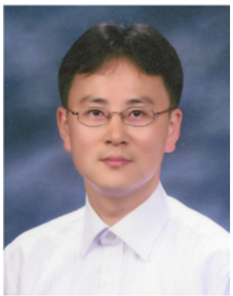
REFERENCES

1. G. Zhang, F. Yu and R. Wang, *Pet. Coal*, **51**, 196 (2009).
2. J. M. Campos-Martin, M. C. Capel-Sanchez, P. Perez-Presas and J. L. G. Fierro, *J. Chem. Technol. Biotechnol.*, **85**, 879 (2010).
3. L. C. Caero, *Oxidative desulfurization (ODS) of aromatic sulfur compounds to obtain ultra low sulfur fuels*, SciTopics, 2010, http://www.scitopics.com/Oxidative_Desulfurization_ODS_of_aromatic_sulfur_compounds_to_obtain_Ultra_Low_Sulfur_Fuels.html.
4. R. Gatan, P. Barger and V. Gembicki, *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.*, **49**, 577 (2004).
5. C. Song, *Catal. Today*, **86**, 211 (2003).
6. I. V. Babich and J. A. Moulijn, *Fuel*, **82**, 607 (2003).
7. B. Pawelec, R. M. Navarro, J. M. Campos-Martin and J. L. G. Fierro, *Catal. Sci. Technol.*, **1**, 23 (2011).
8. C. Song and X. Ma, *Appl. Catal.-B. Environ.*, **41**, 207 (2003).
9. C. Song and X. Ma, *Int. J. Green Energy*, **1**, 167 (2004).
10. T.-W. Kim, M.-J. Kim, F. Kleitz, M. M. Nair, R. Guillet-Nicolas, K.-E. Jeong, H.-J. Chae, C.-U. Kim and S.-Y. Jeong, *ChemCatChem*, **4**, 687 (2012).
11. X. Ma, K. Sakanishi and I. Mochida, *Ind. Eng. Chem. Res.*, **33**, 218 (1994).
12. S. Otsuki, T. Nonaka, N. Takashima, W. Qian, A. Ishihara, T. Imai and T. Kabe, *Energy Fuels*, **14**, 1232 (2000).
13. O. Gonzlez-Garca and L. Cedeo-Caero, *Catal. Today*, **148**, 42 (2009).
14. J. Zhang, X. Bai, X. Li, A. Wang and X. Ma, *Chinese J. Catal.*, **30**, 1017 (2009).
15. A. Takahashi, F. H. Yang and R. T. Yang, *Ind. Eng. Chem. Res.*, **41**, 2487 (2002).
16. A. J. Hernndez-Maldonado and R. T. Yang, *Ind. Eng. Chem. Res.*, **42**, 123 (2002).
17. D. Wang, E. W. Qian, H. Amano, K. Okata, A. Ishihara and T. Kabe, *Appl. Catal.-A. Gen.*, **253**, 91 (2003).
18. D. Chapados, S. E. Bonde, W. L. Gore, G. Dolbear and E. Skov, AM-00-25, NPRA 2000 Annual Meeting (2010).
19. R. E. Levy, A. S. Rappas, S. J. DeCanio and V. P. Nero, AM-01-10, NPRA 2001 Annual Meeting (2001).
20. M. Cullen and A. Avidan, AM-01-55, NPRA 2001 Annual Meeting (2001).
21. F. Liotta and Y. Han, AM-03-23, NPRA 2003 Annual Meeting (2003).
22. R. D. Key, M. D. Ackerson, M. S. Byars, J. Laurent and J. Hallock, AM-03-11, NPRA 2003 Annual Meeting (2003).
23. D. Tuli, *19th World Petroleum Congress, June 29 - July 3, Madrid, Spain* (2008).
24. J. M. Campos-Martin, G. Blanco-Brieva and J. L. G. Fierro, *Angew. Chem., Int. Ed.*, **45**, 6962 (2006).
25. F. Zannikos, E. Lois and S. Stournas, *Fuel Process. Technol.*, **42**, 35 (1995).
26. Y. Shiraishi, K. Tachibana, T. Hirai and I. Komasawa, *Ind. Eng. Chem. Res.*, **41**, 4362 (2002).
27. P. De Filippis and M. Scarsella, *Energy Fuels*, **17**, 1452 (2003).
28. S. H. Ali, D. M. Hamad, B. H. Albusairi and M. A. Fahim, *Energy Fuels*, **23**, 5986 (2009).
29. Y. Shiraishi, H. Hara, T. Hirai and I. Komasawa, *Ind. Eng. Chem. Res.*, **38**, 1589 (1999).
30. T. Hirai, Y. Shiraishi, K. Ogawa and I. Komasawa, *Ind. Eng. Chem. Res.*, **36**, 530 (1997).
31. K. Yazu, T. Furuya, K. Miki and K. Ukegawa, *Chem. Lett.*, **32**, 920 (2003).
32. F. Al-Shahrani, T. Xiao, S.A. Llewellyn, S. Barri, Z. Jiang, H. Shi, G. Martinie and M. L. H. Green, *Appl. Catal.-B.Environ.*, **73**, 311 (2007).
33. L. Hao, S. Benxian and X. Zhou, *Pet. Sci. Technol.*, **23**, 991 (2005).
34. L. Chen, S. Guo and D. Zhao, *Chin. J. Chem. Eng.*, **15**, 520 (2007).
35. W. F. de Souza, I. R. Guimares, M. C. Guerreiro and L. C. A. Oliveira, *Appl. Catal.-A. Gen.*, **360**, 205 (2009).
36. G. Yu, S. Lu, H. Chen and Z. Zhu, *Carbon*, **43**, 2285 (2005).
37. G. Yu, S. Lu, H. Chen and Z. Zhu, *Energy Fuels*, **19**, 447 (2004).
38. X. L. Zhou, Q. Tan, G. X. Yu, L. F. Chen, J. A. Wang and O. Novaro, *Kinet. Catal.*, **50**, 543 (2009).
39. D. Borah, M. K. Baruah and I. Haque, *Fuel*, **80**, 1475 (2001).
40. M. Te, C. Fairbridge and Z. Ring, *Appl. Catal.-A. Gen.*, **219**, 267 (2001).
41. K. Yazu, Y. Yamamoto, T. Furuya, K. Miki and K. Ukegawa, *Energy Fuels*, **15**, 1535 (2001).
42. R. Wang, G. Zhang and H. Zhao, *Catal. Today*, **149**, 117 (2010).
43. S. Mondal, Y. Hangun-Balkir, L. Alexandrova, D. Link, B. Howard, P. Zandhuis, A. Cugini, C. P. Horwitz and T. J. Collins, *Catal. Today*, **116**, 554 (2006).
44. J. Lai and G. Luo, *Pet. Sci. Technol.*, **24**, 1357 (2006).
45. J. Shen, H. P. Li and H. Zhao, *Pet. Sci. Technol.*, **26**, 2182 (2008).
46. X. Jiang, H. Li, W. Zhu, L. He, H. Shu and J. Lu, *Fuel*, **88**, 431 (2009).
47. D. Huang, Z. Zhai, Y. C. Lu, L. M. Yang and G. S. Luo, *Ind. Eng. Chem. Res.*, **46**, 1447 (2007).
48. C. Komintarachat and W. Trakarnpruk, *Ind. Eng. Chem. Res.*, **45**, 1853 (2006).
49. H. Mei, B. W. Mei and T. F. Yen, *Fuel*, **82**, 405 (2003).
50. D. Huang, Y. J. Wang, L. M. Yang and G. S. Luo, *Ind. Eng. Chem. Res.*, **45**, 1880 (2006).
51. O. Etemadi and T. F. Yen, *Energy Fuels*, **21**, 2250 (2007).
52. J. M. Campos-Martin, M. C. Capel-Sanchez and J. L. G. Fierro, *Green Chem.*, **6**, 557 (2004).
53. L. Hongying, J. Gao, Z. Jiang, F. Jing, Y. Yang, G. Wang and C. Li, *J. Catal.*, **239**, 369 (2006).
54. D. Huang, Y. C. Lu, Y. J. Wang, L. Yang and G. S. Luo, *Ind. Eng. Chem. Res.*, **47**, 3870 (2008).
55. C. Li, Z. Jiang, J. Gao, Y. Yang, S. Wang, F. Tian, F. Sun, X. Sun, P. Ying and C. Han, *Chem.-A Eur. J.*, **10**, 2277 (2004).
56. A. Chica, A. Corma and M. E. Dine, *J. Catal.*, **242**, 299 (2006).
57. D. Liu, J. Gui, Y.-K. Park, S. Yang, Y. Gao, X. Peng and Z. Sun, *Korean J. Chem. Eng.*, **29**, 49 (2012).
58. L. Tang, G. Luo, L. Kang, M. Zhu and B. Dai, *Korean J. Chem. Eng.*, **30**, 314 (2013).
59. S. Otsuki, T. Nonaka, W. Qian, A. Ishihara and T. Kabe, *Sekiyu Gakkaishi*, **44**, 18 (2001).
60. J. A. Kocal, *Process for the desulfurization of a hydrocarbonaceous oil*, UOP LLC, US Patent 6,277,271 (2001).
61. J. A. Kocal and T. A. Brandvold, *Removal of sulfur-containing compounds from liquid hydrocarbon streams*, UOP LLC, US Patent

6,368,495 (2002).
62. L. J. Karas, Y. Z. Han and D. W. Leyshon, *Organosulfur oxidation process*, Lyondell, US Patent 2,004,178,122 (2004).
63. Y. Z. Han and D. W. Leyshon, *Desulfurization process*, Lyondell, US Patent 2,005,109,677 (2005).
64. J. Y. Li, X. R. Zhou, D. F. Zhao and C. X. Zhao, *J. Fuel Chem. Technol.*, **34**, 249 (2006).
65. X. Zhou, C. Zhao, J. Yang and S. Zhang, *Energy Fuels*, **21**, 7 (2007).
66. E. L. Kyle and L. V. Jennifer, *Oxidative desulfurization using a titanium (IV) catalyst and organohydroperoxides*, US Patent 8,283,498 (2012).
67. V. Hulea, F. I. Fajula and J. Bousquet, *J. Catal.*, **198**, 179 (2001).
68. A. Ishihara, D. Wang, F. Dumeignil, H. Amano, E. W. Qian and T. Kabe, *Appl. Catal.-A. Gen.*, **279**, 279 (2005).
69. V. V. D. N. Prasad, K.-E. Jeong, H.-J. Chae, C.-U. Kim and S.-Y. Jeong, *Catal. Commun.*, **9**, 1966 (2008).
70. A. Chica, G. Gatti, B. Moden, L. Marchese and E. Iglesia, *Chem.-A Eur. J.*, **12**, 1960 (2006).
71. A. K. Sharipov and V. R. Nigmatullin, *Chem. Tech. Fuels Oils*, **41**, 309 (2005).
72. K.-E. Jeong, H.-J. Chae, C.-U. Kim, S.-Y. Jeong and W.-S. Ahn, *Solid State Phenom.*, **135**, 88 (2008).
73. J. Kim, S. Bhattacharjee, K.-E. Jeong, S.-Y. Jeong and W.-S. Ahn, *Chem. Commun.*, 3904 (2009).
74. L. Cedeño-Caero, H. Gomez-Bernal, A. Fraustro-Cuevas, H. D. Guerra-Gomez and R. Cuevas-Garcia, *Catal. Today*, **133-135**, 244 (2008).
75. Y. Shiraishi, T. Hirai and I. Komasawa, *Ind. Eng. Chem. Res.*, **37**, 203 (1998).
76. Y. Fang and H. Hu, *Catal. Commun.*, **8**, 817 (2007).
77. K.-E. Jeong, C.-S. Cho, H.-J. Chae, C.-U. Kim and S.-Y. Jeong, *J. Nanosci. Nanotechnol.*, **10**, 3547 (2010).
78. G. Gao, S. Cheng, Y. An, X. Si, X. Fu, Y. Liu, H. Zhang, P. Wu and M.-Y. He, *ChemCatChem*, **2**, 459 (2010).
79. H. Song, G. Li and X. Wang, *Micropor. Mesopor. Mater.*, **120**, 346 (2009).
80. L. Kong, G. Li and X. Wang, *Catal. Today*, **93-95**, 341 (2004).
81. M. C. Capel-Sanchez, J. M. Campos-Martin and J. L. G. Fierro, *Energ. Environ. Sci.*, **3**, 328 (2010).
82. S.-T. Yang, K.-E. Jeong, S.-Y. Jeong and W.-S. Ahn, *Mater. Res. Bull.*, **47**, 4398 (2012).
83. P. Wu, T. Komatsu and T. Yashima, *J. Phys. Chem.*, **100**, 10316 (1996).
84. M.-J. Diaz-Cabanas, L. A. Villaescusa and M. A. Camblor, *Chem. Commun.*, 761 (2000).
85. S. Cheng, Y. Liu, J. Gao, L. Wang, X. Liu, G. Gao, P. Wu and M. He, *Chinese J. Catal.*, **27**, 547 (2006).
86. R. Bal, K. Chaudhari, D. Srinivas, S. Sivasanker and P. Ratnasamy, *J. Mol. Catal. A: Chem.*, **162**, 199 (2000).
87. M. C. Capel-Sanchez, G. Blanco-Brieva, J. M. Campos-Martin, M. P. de Frutos, W. Wen, J. A. Rodriguez and J. L. G. Fierro, *Langmuir*, **25**, 7148 (2009).
88. F. O. Berube, A. Khadhraoui, M. T. Janicke, F. Kleitz and S. Kaliaguine, *Ind. Eng. Chem. Res.*, **49**, 6977 (2010).
89. F. Brub, B. Nohair, F. Kleitz and S. Kaliaguine, *Chem. Mater.*, **22**, 1988 (2010).
90. L. C. Caero, J. F, N. A and A. Gutirrez-Alejandre, *Catal. Today*, **116**, 562 (2006).
91. D. S. Shephard, W. Zhou, T. Maschmeyer, J. M. Matters, C. L. Roper, S. Parsons, B. F. G. Johnson and M. J. Duer, *Angew. Chem., Int. Ed.*, **37**, 2719 (1998).
92. K. A. Koyano, T. Tatsumi, Y. Tanaka and S. Nakata, *J. Phys. Chem. B*, **101**, 9436 (1997).
93. Y. V. Subba Rao, D. E. De Vos, T. Bein and P. A. Jacobs, *Chem. Commun.*, 355 (1997).
94. P. Sutra and D. Brunel, *Chem. Commun.*, 2485 (1996).
95. X.-F. Li, H.-X. Gao, G.-J. Jin, L. Chen, L. Ding, H.-Y. Yang and Q.-L. Chen, *J. Mol. Struct.*, **872**, 10 (2008).
96. R. Anwander, I. Nagl, M. Widenmeyer, G. Engelhardt, O. Groeger, C. Palm and T. Roser, *J. Phys. Chem. B*, **104**, 3532 (2000).
97. T.-W. Kim, K.-E. Jeong, H.-J. Chae, C.-U. Kim, S.-Y. Jeong, G. R. Kim, S. H. Oh, J. W. Ryu, D. W. Kim and Y. W. Kim, KR Patent 10-2010-0089590 (2010).
98. C. S. Cho, K. E. Jeong, H. J. Chae, C. U. Kim, S. Y. Jeong and S. G. Oh, *Korean Chem. Eng. Res.*, **46**, 845 (2008).



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