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OXIDATIVE DESULFURIZATION OF ORGANIC SULFUR COMPOUNDS IN THE PRESENCE OF MOLYBDENUM COMPLEX AND ACETONE AS CATALYSTS

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Abstract

The environmental concerns have tightened the strict rules on the quality of fuels especially on the basis of sulfur content. These new requirements of sulfur content of fuels demand the deep desulfurization processes. Currently, the oxidative desulfurization is considered as one of the leading desulfurization methods due to its mild reaction conditions. In this study, the oxidative desulfurization of diesel and gas condensate was conducted using hydrogen peroxide as an oxidizing agent in the presence of molybdenum complex and acetone as catalysts. Additionally the acetone was used as the solvent to extract sulfoxides and sulfones. Tests were carried out in different conditions to compare the effect of time and temperature on the desulfurization percentage. The highest percentage of desulfurization of diesel was obtained at 70°C temperature, within 45 minutes and in an atmospheric pressure, which was about 75%. However, the highest amount of desulfurization for gas condensate at the same time and temperature was 38 %.

Key Words*:* Oxidative Desulfurization; Catalytic Oxidation; Diesel fuel; molybdenum complex catalyst.

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1. Introduction

There was an increasingly rigid legislative regulation on sulfur content of fuels in most western countries during the past two decades. For example, the U.S. Environ-mental Protection Agency limited the sulfur content of most diesel fuels to 15 ppm from a level of 500 ppm in 2006. The similar environmental regulations in Europe forced petroleum industries to reduce the sulfur content for on-road diesel fuels from the level of 350 to 50 ppm by 2005 and to 10 ppm by 2009, while the average amounts of sulfur in crude oil is increasing. Therefore, the refinement of crude oil to obtain final clear products requires desulfurization of the oil.

Hydrodesulphurization (HDS) is widely used to treat fuels for their sulfur content. In the HDS process, hydrogen is used to remove sulfur compounds. To achieve lower sulfur contents in fuels with HDS technology, the high reaction temperature and pressure, large reactor volumes and highly active catalysts are required. As a result, this process demands the advanced design of the reactor and stripping columns; however some of sulfur compounds, namely dibenzothiophenes having alkyl substituent on their 4th and/or 6th positions need harsh process conditions including extremely high temperature and high pressure which considerably push the cost of desulfurization plants up.

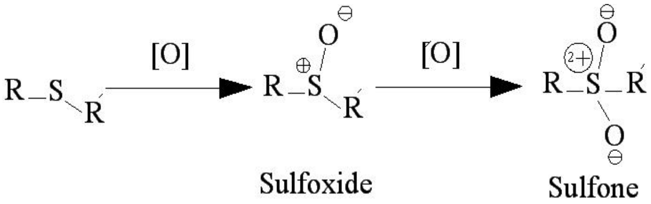
Consequently, an economical alternative to lower the sulfur content of diesel fuel has to be taken into account. It is supposed that Oxidational Desulfurization (ODS) can be an appropriate substitute for the traditional HDS process in which a decrease in total sulfur content of oil leads to a sharp increase in the specific CAPEX and EXPEX per ton of treated crude oil. ODS is considered as one of the leading processes to reduce the total sulfur content of fuels due to its potential advantages over HDS. First, it requires no hydrogen, and, second, this process can be carried out at relatively mild conditions (usually 313-373 K and 0.1-0.2 MPa).

In fact, the ODS is a kind of desulfurization technology in which oxidants oxidize organic sulfur and the reaction products are eliminated by absorption or extraction. ODS is conducted at atmospheric pressure where temperature is usually below 100ºC. Regarding the recent studies, oxidative desulfurization can reduce the sulfur content of diesel and gasoline with 1500 ppm to less than 5 ppm while its cost is less than that of traditional hydrotreater plants.

The ODS invariably involves two different steps. The first step is the sulfur oxidation, which changes the nature of the sulfur compounds. The second step is the sulfur removal using liquid extraction or adsorption at the end. There are plenty of studies investigating the oxidative desulfurization of oil fractions, namely, gasoline, and diesel fuel.

In the study conducted by G. Zhang, the ODS methods were divided into the several categories: H_2O_2 oxidation method, organic oxidant method, photochemical oxidation method and oxidation involving the use of plasma or ultrasound [1]. Unipure Company (USA) has developed ASR process based on oxidational removal of organic sulfur compounds from oil and petroleum fractions. The Unipure's ASR process is able to convert medium and high sulfur crude oil into sweet crude oil containing less than 0.5 % sulfur content. In addition to sulfur treatment of crude, the ASR reduces the viscosity of crude and raises its API gravity while this process requires no hydrogen, no heaters and the energy consumption is considerably low [2-3].

A general view of a reaction of sulfide oxidation to sulfoxide and then to sulfone is as follows:



There are some differences between the properties of sulfoxides and sulfones and organic sulfur compounds that facilitate desulfurization. The sulfoxides and sulfones have more polarity than the unoxidized sulfur compounds, which raises selectivity during solvent extraction. Additionally, the C–S bond's strength is decreased when the sulfur is oxidized. Therefore, it is easier to remove the oxidized sulfur compounds.

Sulfides are readily oxidized to sulfoxides by a variety of oxidizing agents including peroxy organic acids, hydroperoxides, nitrogen oxides, peroxy salts and ozone, sodium periodate ($NaIO_4$), hydrogen peroxide or alkyl hydroperoxides etc. Based on conducted studies, ODS process involves two main steps. The first step is the sulfur oxidation, which changes the nature of the sulfur compounds. The second step is the removal of oxidized sulfur. Recently, there have been some research and review papers comprehensively investigating these two steps of ODS process [4-6].

The main aspects of the patent literature on the first step of ODS of heavy oil are divided into following groups.

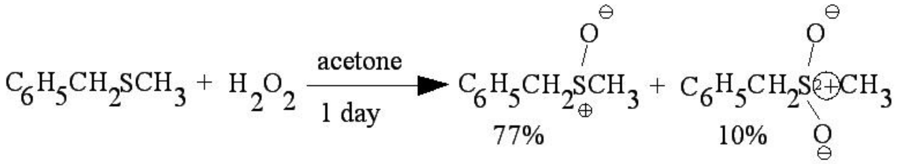
2. The Step of Oxidization of Organic Sulfur Compounds

2.1 Oxidizing organic sulfur compounds using miscellaneous oxidizing agents

There are plenty of various methods of oxidation of organic sulfur compounds using various oxidants like nitrogen dioxide, chlorine oxide, porphyrin complexes, etc. that can provide oxygen atoms for the sulfur in mercaptans, thiols, sulfides and so forth [8]. Photochemical oxidation and Ultrasound oxidation are two less known oxidization methods investigated in several research papers. These methods' oxidation mechanisms are similar to the other oxidation methods; however, instead of the thermal energy; energy is supplied by light or ultrasound. The first method is just viable for light oil and the second one cannot be scaled up to use in industrial scales [8].

2.2 Oxidizing organic sulfur compounds using hydrogen peroxide (H_2O_2)

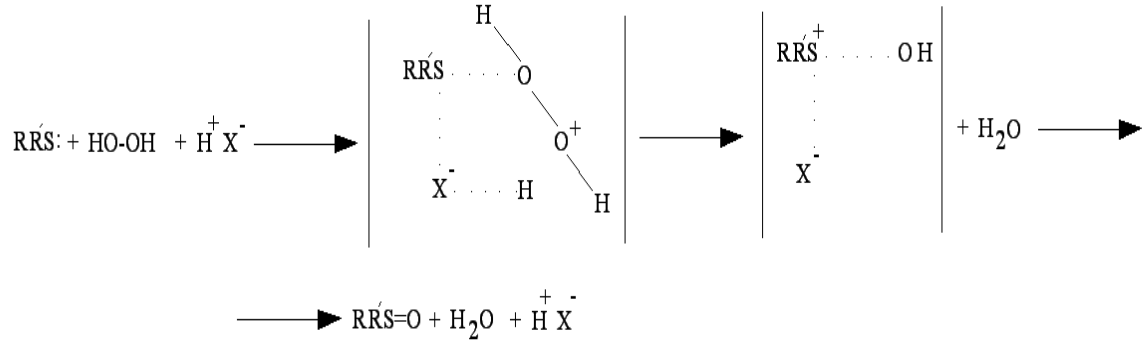
Regarding the various research in ODS field, one can realize that the best oxidizing agent for ODS processes is hydrogen peroxide in a polar solvent or acid (acetic acid or acetone) used as a catalyst. However, even under lab conditions, besides sulfoxide, usually a certain quantity of sulfone is produced following this reaction [1, 5, 6-7]:



The sufficient amounts of catalysts can accelerate reaction and raise the oxidation efficiency. It is known that the organic acid and heteropolyoxometalates are catalysts used widely in ODS process.

2.2.1 H_2O_2-organic acid

H_2O_2 in short-chain carboxylic acids (formic acid or acetic acid) as catalysts is considered as the common oxidative desulfurization system for the fuel oil. The mechanism of sulfide oxidation to sulfoxides using H_2O_2-organic acid is not studied sufficiently; however, the potential mechanism is a heterolytic electrophyl interaction where H^+X^- is a polar solvent. Based on this mechanism, H_2O_2 fist reacts with organic acid quickly and generates peroxide acid, and then the acid reacts with nonpolar sulfur compounds and generates relative sulfone or sulfoxide. The oxidation is conducted at low temperatures, typically at 50 °C for 6 h [1, 7-8]:



An example of the use of H_2O_2, as an oxidizing agent, is Otsuki et al. research in which they applied H_2O_2 as an oxidant and formic acid as a catalyst to oxidize the sulfur compounds [9]. However, oxidizing sulfides requires a substantial amount of oxidizing agent that makes this process economically unfeasible. Therefore, it is suggested that using a proper catalyst will make the oxidization of sulfide compounds with H_2O_2 viable.

2.2.2 H_2O_2-heteropolyoxometalates or metal-based catalyst

One of the catalysts investigated in some research articles is known as heteropolyoxometalates, which is a solid acid oxidation catalyst with several pluses- a large molecular size, good transmission to name but a few [10-11]. Heteropolyoxometalates, namely tungstophosphoric acid (TPA) was used as a kind of catalyst in the oxidative desulfurization in the literature. In the research conducted by Yazu et al. the organic sulfur such as benzothiophene in octane was oxidized with hydrogen peroxide and TPA catalyst in acetic acid(AcOH)/octane biphasic system. They found, the oxidation reaction happened in AcOH phase, and most of the oxidation products remained in this phase and resulted in the successive removal of sulfur compounds from the octane phase. When the reaction temperature was 50°C, the benzothiophene in the solvent could completely be removed [10]. In addition to these types of catalysts that generate a heterogonous catalytic system, the homogeneous catalysis is currently studied by petroleum industries in ODS field including peroxo complexes of d^0 transition metals such as Ti (IV), V (V), Mo (VI) and W (VI). They are strong electrophiles showing a remarkably high selectivity in oxidation of dialkyl and alkyl aryl sulfides [12]. In a research conducted by A. V. Anisimov et al. it was shown that thiols could be oxidized by hydrogen peroxide in the presence of vanadium, tungsten and molybdenum peroxocomplexes in bi-phase system [13].

2.2.3 H_2O_2- Cooperation of heteropolyoxometalates and phase transfer catalysts

Hydrogen peroxide cannot dissolve in oil phase. Therefore, oil is unable to absolutely access to oxidants in the reaction process, which reduces the reaction speed, and leads to an improper desulfurization and raises the amount of oxidant. Phase transfer catalyst (PTC) can improve the poor contact between oil and an oxidizing agent. This type of catalyst can expedite the reaction between two reactants in two mutually exclusively soluble solvents (liquid - liquid two-phase system or solid - liquid two-phase system). During the reaction, the actual reactants are transferred from one phase to another by catalyst. Consequently, the reaction can be conducted at high rate. Mure Te et al. applied polyoxometalates to catalyze the oxidation of DBT, 4-MDBT and 4, 6 –DMDBT using hydrogen peroxide as oxidant, tetraoctylammonium bromide as a phase transfer catalyst, and toluene as a solvent. The temperature was at 50°C, DBT could be removed above 80% in 30 minutes, and 100% in 90 minutes [11].

2.3 Oxidizing organic sulfur compounds using Organic Hydroperoxides

Moreover, organic hydroperoxides can be used as oxidants in ODS processes. The most important advantage of this oxidizing agent is related to the simple reactor design. Additionally, organic oxidants are oil-soluble and in comparison with H_2O_2, which is a water-soluble agent, they require a shorter time to mix with the oil. The most widely hydroperoxide employed is t-butylhydroperoxide (TBHP) in the presence of various catalysts like Mo catalysts supported on Al_2O_3. The ODS process based on this oxidant was patented by Lyondell Chemicals and EniChem/UOP. A major drawback is the high cost of t-butylhydroperoxide, and the waste treatment of sulfone and the t-butyl alcohol by-product generated [7,15].

2.4 Oxidizing organic sulfur compounds using Air oxygen

The use of expensive oxidants reaction systems results in biphasic systems that makes the ODS process an unfavorable technology. The oxygen of air is considered as an inexpensive, appealing and green oxidant for ODS process which is easily accessible. The oxidization of sulfur compounds of fuel using air oxygen leads to the production of the hydroperoxide species that is a key intermediate produced in situ by the oxygen. This process proceeds at a temperature, which is usually less than 200°C and near to the atmospheric pressure and is called "autoxidation". Autoxidation can be conducted in the absence or presence of catalyst. In recent studies, the oxidative desulfurization was conducted with air in an acetone solution and using copper (II) phenolates as a catalyst exhibited the high performance. Furthermore, the ODS process was done with oxygen using Fe (III) salts [Fe (III) nitrate and Fe (III) bromide] as catalysts to desulfurize thiophenic sulphur compounds or transition metal (Cobalt, Nickel, Copper) catalyzes co-oxidation of organic sulphur compounds and aldehydes [18]. Additionally, in some studies the ODS with air was done without catalyst using a high polarity solvent to dissolve the oxidized products [19]. However, high solvent consumption, the use of organic acid and expensive catalytic systems do not allow considering this process adaptable to an industrial process [8, 14-15, 17-19].

3. The Step of Removal of Oxidization Products

The second step of ODS process is the removal of the oxidized compounds. There are some research articles explaining two general methods to eliminate the oxidized sulfides including contacting them with a selective extraction solvent or adsorption [1, 7-8,15].

A process of extraction of oxidation products (sulfoxides) from oxidate can be developed based on a wide variety of polar solvents and binary systems, namely methanol, *N, N*-dimethyl-formamide, dimethylsulfoxide (DMSO), dimethylformamide (DMF) and acetonitrile [7]. However, the most efficient and available extractive agent is an aqueous solution of acetone .Water is added into the solvent in order to increase the solution polarity, solvent selectivity and to provide the deep extraction of sulfoxides from oxidate. These solvents are available and relatively inexpensive. Technologic advantages of their use are connected with sufficiently high selectivity of extraction of target components, easy regeneration from extractive and raffinate solutions.

The advantage of acetone utilization in the oxidation is also related to the fact that an aqueous solution of acetone can be used on the subsequent process stages for sulfoxides extraction from oxidate. The sulfoxides extraction can reach up to 90% and their content in the extracted product is up to 10% mass. Besides, acetone can be easily regenerated from the extraction solution and sent as a recycle stream to the oxidization reactor and extractive column, while sulfoxides after settling are separated from the aqueous phase. The absence of a stage of water-wash of the oxidate for acid components and possibility of flexible control of acetone consumption on the extraction stage are considered as the main preferences of this solvent.

4. The Selection of The Most Efficient Method of ODS

Although several studies have been conducted in the field of ODS and its benefits are obvious in comparison with other processes used to remove the sulfur compounds of oil fractions, commercial technologies of ODS of petroleum fractions have not yet been developed due to some obstacles including:

- The serious influence of fractional and chemical composition of feed on process parameters and results
- The need for an accurate design of a process including two stages of oxidation and extraction or adsorptive removal of oxidation products
- The need for an accurate selection of oxidizer, catalyst and extractant, through they have to provide ODS with the highest efficiency compared with other desulfurization methods, especially HDS

Inevitably, each of the ODS methods has some merits and demerits. The high reactivity and availability of hydrogen peroxide make it as a major oxidizer of the organic sulfur compounds. Therefore, in spite of a number of drawbacks- explosiveness, low selectivity of oxidation and the insolubility of aqueous H_2O_2 in hydrocarbons- it can be used commercially. The peracids are considered as very powerful oxidizing agents; however, these compounds are highly corrosive and amount of oxidizing agent is significantly high compared with that of the desulfurized product, which makes this process uneconomical. The hydroperoxides are oil-soluble oxidizers however, the use of hydroperoxides leads to an increase in the acidity of product due to intensive oxidization of hydrocarbon. Besides, it can reduce the yield of sulfoxide through their oxidation to sulfones and sulfo acids. The rise in sulfone content of a raffinate results in an increase in the total sulfur content of the raffinate, because the selectivity of sulfone extraction with a polar solvent is lower than that of sulfoxide [14-15]. The oxygen of air can be an ideal oxidant in the ODS process of oil, which is free, readily available, portable, and environmentally friendly. However, the temperature of this process is remarkably high and requires various types of solvents, catalysts and advanced instrumentation while this method is not as selective as some other oxidization methods [18].

To summarize, based on this short review on the ODS processes, the most effective methods of ODS can be categorized into 3 general groups:

1- Oxidization using hydrogen peroxide as an oxidant, acetone, acetic acid/ peroxo complexes catalyst with subsequent extraction with the acetone as a solvent
2- Oxidization using hydroperoxide solutions with subsequent extraction with an aqueous solution of organic solvent
3- Oxidation using air oxygen in acetone medium with catalytic additives of copper phenolate (phthalate) or cobalt phtalocyanine and extraction of sulfoxides with the same solvent

Due to preferences of the first ODS method exhibited in several research articles, it was intended to apply the first method to oxidize the sulfides of diesel fuel in this study. To optimize the process parameters, it is essential to study a possibility of increasing oxidation selectivity by adding inhibitors of oxidation hydrocarbons with hydroperoxides and H_2O_2. It is assumed that sulfides of transition metals as well as sulfoxides can be used as inhibitors and returned to the reactor. Sulfoxide recycling in the system will also initiate a basic reaction of organic sulfur compounds oxidation, which will lead to an increase in sulfide conversion and a fall in the product acidity.

The main aim of the present work is to develop a new process of oxidational desulfurization of diesel fuel, which provides a significant increase in oxidation rate and organic sulfur compound conversion, under relatively mild conditions. To conduct the tests, the relatively inexpensive and easily accessible materials were used as reactants-oxidizers and catalysts. The key innovation of this study is related to the use of two types of catalysts in the ODS of diesel and gas condensate, simultaneously. It is supposed these catalysts can raise the desulfurization percentage of these fuels.

5. Experimental method

In the present study, based on information elicited from the relevant literature, the hydrogen peroxide was used as an oxidizing agent to oxidize the sulfides of diesel fuel and gas condensate. The experiments of oxidation with hydrogen peroxide were conducted in acetone and peroxo complexes of molybdenum as catalysts, followed by extraction with the same solvent.

In the first section, the diesel fraction of oil with boiling point range of (180-3500°C) with total sulfur content of 0.49% mass, the sulfur content as sulfides of 0.3% mass was used as a feed in the experimental work. Total sulfur content was determined using "Spectroscan", equipped with X-ray fluorescent detector and the amount of sulfur content as sulfides was measured by potentiometric titration. The second section was related to oxidative desulfurization of demercaptanized gas condensate with 0.77 % mass of total sulfur containing 900 ppm of RSH and 0.29 % mass of sulfides.

Oxidational desulfurization was carried out with hydrogen peroxide 35% over catalysts and was followed by extraction of sulfoxides from the oxidate using acetone. The proportion of acetone to feed was 1.0% volume. First, the acetone was applied as catalyst and then the peroxo complex of molybdenum catalyzed this process.

Afterwards, the peroxo complex of molybdenum salt and oxide, in the form of solution in hydrogen peroxide was used as catalyst. The proportion of catalyst to the feed was 0.001% mass. The use of two types of catalysts exerted two mechanisms of catalytic oxidation: the formation of oxi hydroperoxide under the influence of acetone and the formation of intermediate active metal peroxo complexes using peroxo complexes of molybdenum. Furthermore, the presence of a polar solvent in this system exerted positive influence on distribution of a solvent and peroxo complexes in the hydrocarbon phase. The combined influence of these factors resulted in an increase in oxidation selectivity and sulfide conversion. The oxidation process was carried out at two temperatures of 60-70°C ranging 30 to 45 minutes. Afterwards, the, sulfoxide was extracted from the oxidate with an aqueous solution of acetone. Extraction with an aqueous solution of acetone was conducted at 50°C and the mole ratio of H_2O_2 to sulfides was 1.2. The low-molecular weight mercaptans C1-C3 content in the treated gas condensate did not exceed 30 ppm,

6. Results and Discussion

The results of the experiments of oxidative desulfurization of diesel and gas condensate are tabulated in Tables 1 and 2.

Table 1 Results of oxidative desulfurization of diesel

Temperature, ºC	Oxidation Time, min.	Catalyst	Extractant-Oxidate Ratio	S_{total} Raffinate, % Mass	Desulfurization, %
60	45	-	3(vol.)	0.43	12
70	45	$(CH_3)_2CO$	3(vol.)	0.27	45
60	45	$(NH_4)_2MoO_4$	3(vol.)	0.31	37
60	30	$(NH_4)_2MoO_4+(CH_3)_2CO$	3(vol.)	0.31	41
70	45	$(NH_4)_2MoO_4+(CH_3)_2CO$	3(vol.)	0.43	47
			4(Vol.)	0.12	75.3

The first set of experiments related to ODS of diesel is shown in table 1. According to Table 1, the non-catalytic oxidation of diesel fuel predictably resulted in the lowest amount of desulfurization. The use of acetone as a catalyst showed the higher desulfurization compared with the test in which peroxo complexes of molybdenum was applied as a catalyst.

Afterwards, the peroxo complexes of molybdenum in combination with acetone catalyzed desulfurization process of diesel fuel that significantly raised the sulfide conversion. According to table 1, the use of these two catalysts simultaneously, even at short oxidation time resulted in the higher desulfurization of diesel.

Raising the oxidation temperature to 70°C and the oxidation time to 45 minutes, one could realize that the oxidation of sulfide showed an appropriate outcome and reached 47%. The highest amount of desulfurization of diesel was obtained at 70°C temperature within 45 minutes with the extractant-oxidate ratio of 4 which was over 75 %.

The second set of tests concerned with ODS of demercaptanized gas condensate which are summarized in Table2.

Table 2 Results of oxidative desulfurization of demercaptanized gas condensate

Oxidizer feed	Temperature °C	Oxidation time min	Catalyst consumption, ppm	Extraction with acetone at 50°C	Product characteristic		Desulphurization degree, %
				Water in acetone, % mass	S_{total} ppm	S_{RSH} PPM	
1	70	30	50	10	0.6	146	22
1.5	70	45	100	10	0.48	27	38

According to Table 2 the highest amount of desulfurization of condensate was obtained at the highest temperature and time period of ODS which was 38%. The results of two sets of experiments suggested that ODS of diesel revealed more promising results in comparison with condensate that might be related to the type of sulfur compounds of these two different hydrocarbons. In fact the process of ODS with hydrogen peroxide as an oxidizing agent and two catalysts is effective for hydrocarbons including the higher amount of sulfur compounds as sulfides.

7. Conclusions

In this study, the oxidative desulfurizations of diesel fuel and gas condensate were effectively conducted using hydrogen peroxide as an oxidizing agent. Molybdenum complex in combination with acetone were used as catalysts. An increase in ODS process time and temperature led to a fall in sulfur content of hydrocarbons. Moreover, another crucial and effective factor in removing organic sulfur compounds using ODS was related to the ratio of extractant to oxidate that could heighten the desulfurization percentage in this process. It was observed that using these two types of catalysts can exert two different types of oxidation mechanism which can substantially reduce the organic sulfur compounds of diesel. However this process demonstrated the lower amount of desulfurization for condensate at the same operation conditions due to its lower amount of sulfur compounds as sulfides.

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References

[1] Zhang, G.; Yu, F.; Wang, R.; Petroleum & Coal, 2009, 51, 196.
[2] Levy, R. E.; Rappas, A. S.; Nero, V. P.; De Canio, S. J.; presented at 17th World Petroleum Congress, Rio de Janeiro, Brazil, 2002
[3] Liu, K.; Song, C.; Subraman, V.; Hydrogen and Syngas Production and Purification Technologies, John Wiley & Sons, New Jersey, 2009, p. 296
[4] Bahrami, K.; Khodaei, M. M.; J. Org. Chem., 2010, 75, 6208
[5] Golchoubian, H.; Hosseinpoor, F.; Molecules, 2007, 12, 304
[6] Smith, M. B; Organic Synthesis, Academic Press, Elsevier Inc., 1946, p. 333
[7] Campos-Martin, J.M.; Capel-Sanchez, M.C.; Perez-Presas, P.; Fierro, J.L.G.; J. Chem. Technol. Biotechnol., 2010, 85, 879.
[8] Javadli, R.; de Klerk, A.; Appl. Petrochem. Res., 2012, 1, 3.
[9] Otsuki, S.; Nonaka, T.; Takashima, N.; Energy Fuels, 2000, 14, 1232.
[10] Yazu, K.; Sato, S.; Sugimoto, Y.; J. Jpn. Pet. Inst., 2007, 50, 329.
[11] Te, M.; Fairbridge, C.; Ring, Z.; Appl. Catal., A, 2001, 219, 267.
[12] Chemistry of Functional Groups series: The Chemistry of Peroxides, Rappoport, Z.; Marek, I.; ed.; John Wiley and Sons Ltd., West Sussex, 2006, p. 1095.
[13] Anisimov, A. V.; Fedorova, E. V.; Lesnugin, A. Z.; Senyavin, V. M.; Aslanov, L.A.; Rybakov,V. B.; Tarakanova, A. V.; Catal. Today, 2003, 78, 319.
[14] Wang, D.; Qian, E. W.; Amano, H.; Okata, K.; Ishahara, A.; Kabe, T.; Appl. Catal., A, 2003, 253, 91.

[15] Sundararaman, R.; Ma, X.; Song, C.; Ind. Eng. Chem. Res., 2010, 49, 5561.
[16] Vakhitova, L. N.; Skrypka , A. V.; Savelova, V. A.; Popov, A. F.; Panchenko, B. V.; Theor. Exp. Chem., 2005, 41, 98.
[17] Fox, B. R.; Ph.D. thesis, University of Oregon (the US), 2011.
[18] Javadli, R.; M.S. these, University of Alberta (Canada), 2011.
[19] Xu, X.; Moulijn, J. A.; Ito, E.; Wagemans, R.; Makkee, M.; Chem. Sus. Chem., 2008, 1, 817.

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