

## REVIEW

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# Performances, kinetics and mechanisms of catalytic oxidative desulfurization from oils

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Ultra-deep desulfurization technologies are critical for cleaner oils and consequent better air quality. Earlier efforts in this field focused on specific catalysts and their catalytic efficiencies, while current interest has shifted to the differences between homogenous and heterogeneous catalysis systems applied in catalytic oxidation desulfurization (ODS) as well as their advantages and disadvantages. In this review, catalysts using various supports were described and their catalytic activities in total oxidation of sulfur compounds were evaluated and commented meanwhile, taking hydroperoxide as oxidant. Then, the effects of reaction parameters on catalyst activities and the kinetics and mechanisms that were used for ODS from oils were reviewed. Under the same conditions, heterogeneous catalysts performed better than homogeneous catalysts. Leaching of active components, existence of N-containing compounds and excessive reaction temperature would deactivate catalysts in ODS. Besides, power-law kinetics equations, Langmuir–Hinshelwood mechanism, and “nucleophilic attack” reaction mechanism” will provide in-depth analysis of desulfurization process and catalysts deactivation. Future research needs on ODS are proposed including the development of novel carrier materials, the optimization of acid sites distribution and the better understanding of deep reaction mechanisms.

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## 1. Introduction

Sulfur (S) is abundantly present in oils, and the average total S content in oils ranges from 100 ppmw to 33 000 ppmw.<sup>1–3</sup> The main types of S-containing organic compounds present in oils are large molecular thiophene including dibenzothiophenes (DBT), alkyl DBT without substitution at 4 and 6 position (~20%), alkyl benzothiophenes (~39%) and alkyl DBT with substitution at 4 or 6 position (~26%).<sup>4</sup> Emissions of sulfur oxides (SO<sub>x</sub>, x = 2, 3) from combustion of fuels are known to be a main source of air pollution, leading in particular to the



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formation of acid rain and acid smog.<sup>5-7</sup> For instance, SO<sub>2</sub> in the lower atmosphere can easily react with moisture in the air, and then acid formed which may accelerate the erosion of historical buildings, damage the foliage,<sup>8,9</sup> or lower the pH of lakes with low buffer capacities and consequently endanger the ecosystem.<sup>10-15</sup> Moreover, inhaling toxic air pollutants could endanger human health severely *via* damaging the lungs and respiratory systems. In 2012, 19.48% of death from respiratory system diseases could be attributed to SO<sub>x</sub> in Malaysia.<sup>16</sup>

In order to minimize the negative environmental and health effects, governments worldwide are adopting more stringent regulations to reduce sulfur emissions *via* enforcing applications of ultra-low sulfur concentration of fuels. Sulfur limitation in diesel has been decreased from 500 to 15 ppmw in average since June 2006 by the United States Environmental Protection Agency (EPA).<sup>17</sup> Japan and EU have established permissible sulfur content in diesel fuel as low as 10 ppmw.<sup>18,19</sup> More and more stringent regulations on sulfur emissions could be expected worldwide in the near future.<sup>20-22</sup> Therefore, investigations on more effective desulfurization technologies have been paid close attention.<sup>23</sup>

The desulfurization technologies can be mainly categorized into two types:<sup>24,25</sup> traditional HDS technologies and alternative desulfurization technologies including extraction,<sup>26-28</sup> adsorption,<sup>29-33</sup> chemical desulfurization,<sup>34-36</sup> oxidation<sup>37-40</sup> and bio-desulfurization.<sup>41-44</sup> The traditional HDS technology is the most widely used method to convert organic sulfur into hydrogen sulfide. However, it is hard to meet the very stringent environmental regulations due to the severe hydrotreating operating conditions such as high pressures, high temperatures, and high hydrogen consumptions. Moreover, it is especially expensive and ineffective for the treatment of DBT, BT and their derivatives.<sup>18,28</sup> Meanwhile, the alternative desulfurization technologies have recently emerged as commercially competitive processes, of which the catalytic oxidation desulfurization (ODS), has been proved to be one of the most promising processes for deep desulfurization from oils due to its highly selective conversion of organic sulfur to corresponding sulfone under mild reaction conditions.<sup>30,35</sup>

ODS that can meet the sulfur regulations provides several advantages over other desulfurization technology, such as milder reaction conditions (usually 1–2 atm and 40–100 °C),



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higher selectivity, lower capital cost, and less hydrogen consumption. The refractory sulfur compounds can be transformed into water-soluble products in ODS, *i.e.* thiophene and its lower polarity compounds can be converted to the corresponding sulfoxides/sulfones with higher polarity by strong oxidants, then the sulfones can easily be absorbed or extracted by polar solvents (methanol, acetonitrile, *N,N*-dimethylformamide, *etc.*) to attain high desulfurization efficiency.

Potential catalytic oxidative desulfurization methods to produce low sulfur fuel oils involved various types of oxidants and catalysts, such as H<sub>2</sub>O<sub>2</sub>/formic acid,<sup>45</sup> H<sub>2</sub>O<sub>2</sub>/acetic acid,<sup>46</sup> H<sub>2</sub>O<sub>2</sub>/inorganic solid acids,<sup>47</sup> H<sub>2</sub>O<sub>2</sub>/heteropolyacids,<sup>39,48</sup> ozone/heterogeneous catalysts,<sup>49</sup> NO<sub>2</sub>/heterogeneous catalysts,<sup>50</sup> O<sub>2</sub>/aldehyde/cobalt catalysts<sup>51</sup> and *tert*-butylperoxides/heterogeneous catalysts.<sup>52</sup> Among the stoichiometric reagents, H<sub>2</sub>O<sub>2</sub> is considered the most promising oxidizing agent in terms of selectivity, safety, product quality, process economics and environmental benign properties.<sup>53</sup> When H<sub>2</sub>O<sub>2</sub> is used in this process, it occasionally needs to be promoted by the catalyst and the corresponding carboxylic acid, for example, acetic or formic acid, to form a peroxyacid.<sup>54,55</sup> Further benefits can be achieved using an efficient catalyst to activate the H–O–O–H bonds through forming active oxygen species.<sup>56</sup> V. Hulea *et al.*<sup>57</sup> used H<sub>2</sub>O<sub>2</sub> as oxidant in several catalysis systems, obtained the catalytic oxidation efficiency exceeding 95% for all tests. Therefore, the importance of hydroperoxide as a “green” oxidant in ODS has grown considerably.

Besides, numerous studies have proved that potential ODS process are operated under either homogenous or heterogeneous catalytic conditions. The homogenous catalysis systems are remarkably efficient, however, the common drawback they share is difficult to separate and reuse the catalysts. Therefore, the application of heterogeneous catalysts in catalytic oxidation desulfurization process is of particular relevance from the environmental point of view, because it can reduce the leaching of metal in residues as well as favour the reuse and recovery of the catalyst itself for continuing transformations.

Up to now, researchers have successfully developed virtually-diversified and highly-selective heterogeneous catalysts, such as WO<sub>x</sub>/ZrO<sub>2</sub>,<sup>58</sup> WO<sub>3</sub>-SBA-15,<sup>59</sup> titanasilicate<sup>57</sup> *etc.*, and utilized them for decontamination of sewage, detoxification of waste waters in chemical refineries,<sup>60,61</sup> and purification of air. There exist strong interests on the studies about heterogeneous catalysts that capable of producing the future “zero sulfur” fuels and the high-value chemicals.<sup>62,63</sup> The fundamental properties of specific catalysis systems and their catalytic efficiencies have been covered in the latest review articles. However, the review that could systematically analyze and compare homogenous and heterogeneous catalysis systems applied in catalytic oxidative desulfurization of fuel oils is not available in the literatures, as far as we know.

This review paper provides the insightful and systematization analysis of the catalysts that were prepared by different carriers and their performances with hydroperoxide as oxidant at mild conditions. The effects of reaction parameters on catalyst activity and the developed kinetics and mechanism have also been discussed. The following contents are covered in detail: (i) the performances of different homogeneous and

heterogeneous catalysis systems, (ii) the effects of different reaction conditions, (iii) the kinetics model of ODS, and (iv) the mechanism of ODS using different oxidants. The aim of this review is help better understanding the application of various homogeneous and heterogeneous catalysis systems and future research needs.

## 2. Catalysts

To our knowledge, most studies on ODS have focused on the development of oxidant and catalysts for selective oxidation.<sup>56,64–66</sup> The ODS catalysts have been investigated without carriers or using active carbon, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub>, mesoporous silicates, and SBA as the carriers. Taking into consideration the efficiency of catalysts, the influence of active components and nitrogen-containing compounds (N-containing compounds) on the formation of by-products during reaction process, the main goal of these researches is to develop new ODS catalysts with high stability, excellent selectivity, good activity and an easy catalysts recycle method, which make it possible to place traditional HDS catalysts applied in industrial desulfurization. However, since most of the ODS catalysts were just studied in the laboratory, more researches into practical application are needed.

### 2.1. Homogeneous catalysts without carriers

**2.1.1. Formic acid.** Formic acid is one of the main organic acids used in ODS. More recently, Otsuki *et al.*<sup>49</sup> have reported that the reactivity of S-containing compounds for oxidation seemed to correlate well with the electron density on sulfur atom except for the 4-methyldibenzothiophene (4-MDBT) and 4,6-methyldibenzothiophene (4,6-MDBT). The electron densities on sulfur atoms were estimated by molecular orbital (MO) calculations (Table 1), and their rate constants would enhance with the increase of electron density (Fig. 1).

The author proposed an electronic theory about the oxidation of organic S-containing compounds: the thiophene derivatives with electron density ranging from 5.696 to 5.739 could not be oxidized at 50 °C. A vital factor that could not be ignored was the ultimate yields of low sulfur fuel oils, therefore, solvent extraction to separate the oxidation products was not the best way in this system. G. X. Yu *et al.*<sup>67</sup> modified H<sub>2</sub>O<sub>2</sub>/formic acid with activated carbon, investigating the catalytic and absorptive performance of activated carbon as well as the effects of reaction conditions. The results showed that the catalytic oxidation performances of H<sub>2</sub>O<sub>2</sub>/formic acid modified with activated carbon were significantly better than that of H<sub>2</sub>O<sub>2</sub>/formic acid. Mure *et al.*<sup>42</sup> proved that the catalysts' molecular size would play an important role in determining reactivity ordering of DBTs oxidation, leading to a better understanding of the reaction mechanisms for researchers.

**2.1.2. Acetic acid.** Petro Star Inc.<sup>68</sup> first introduced conversion/extraction desulfurization (CED) technology to remove sulfur from diesel fuel in 1996 (Fig. 2). Acetic acid that can react with H<sub>2</sub>O<sub>2</sub> to form the peracetic acid, another organic acid commonly used in ODS. F. Zannikos *et al.*<sup>69</sup> desulfurized

Table 1 Electron densities on sulfur atoms and their rate constants

Sulfur compound	Structure	Formula	Molecular weight	Electron density	$k/\text{L mol}^{-1} \text{min}^{-1}$
Thiophenol		$\text{C}_6\text{H}_6\text{S}$	110.18	5.902	0.270
Diphenyl sulfide		$\text{C}_{12}\text{H}_{10}\text{S}$	186.28	5.860	0.156
4,6-DMDBT		$\text{C}_{14}\text{H}_{12}\text{S}$	212.31	5.760	$0.767 \times 10^{-1}$
4-MDBT		$\text{C}_{13}\text{H}_{10}\text{S}$	198.28	5.759	$0.627 \times 10^{-1}$
DBT		$\text{C}_{12}\text{H}_8\text{S}$	184.26	5.758	$0.460 \times 10^{-1}$
BT		$\text{C}_8\text{H}_6\text{S}$	134.20	5.739	$0.574 \times 10^{-2}$
2,5-DMT		$\text{C}_6\text{H}_8\text{S}$	112.19	5.716	—
2-MT		$\text{C}_5\text{H}_6\text{S}$	98.17	5.706	—
Thiophene		$\text{C}_4\text{H}_4\text{S}$	84.14	5.696	—

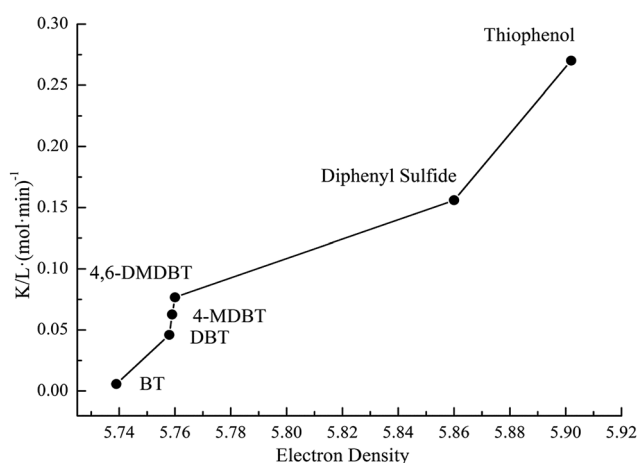


Fig. 1 Relationship between the rate constant  $k$  of the model compounds and their electron densities. The black dots represent the model S-containing compounds in oils.<sup>49</sup>

diesel with  $\text{H}_2\text{O}_2$ /acetic acid system, dissolving the relevant gas oil in acetic acid and heating the mixtures to  $90^\circ\text{C}$ . A solution of 30% aqueous  $\text{H}_2\text{O}_2$  was then added dropwise and with continuous stirring over a period of about 30 min. The molar ratio of

$\text{H}_2\text{O}_2$  to each sulfur equivalent in the oil was 3 : 1. The effects of different solvents on oxidative desulfurization were also studied. When oxidation with simultaneous extraction, results of the test did not show a significant difference in extraction efficiency. The ultimate desulfurization efficiency of diesel in this system was 90% and the quality of diesel in this system would not be damaged.

K. Yazu *et al.*<sup>70</sup> added strong acid  $\text{H}_2\text{SO}_4$  in  $\text{H}_2\text{O}_2$ /acetic acid system. The introduction of  $\text{H}_2\text{SO}_4$  accelerated the oxidation speed of DBTs. The author speculated that the reason might be  $\text{H}_2\text{SO}_4$  played a promoting role in oxidation of acetic acid into

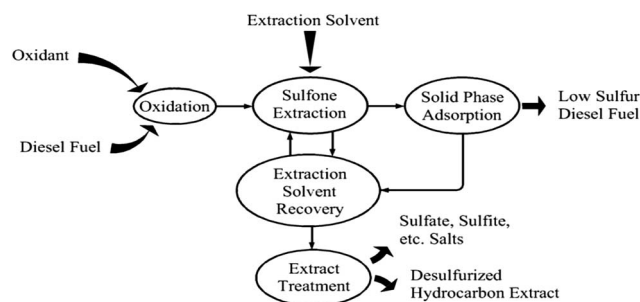


Fig. 2 Simplified diagram of the CED technology.<sup>68</sup>

peracetic acid with  $\text{H}_2\text{O}_2$ . Besides, the experiment of simultaneous removal of sulfur and nitrogen from fuel oils was investigated by Yasuhiro *et al.*<sup>26</sup> And results showed that the sulfur and nitrogen contents of fuel oils were decreased to <0.05 wt% and <22 wt%, respectively, while keeping a high oil recovery yield.

**2.1.3. Heteropolyacid.** Heteropolyacid is also a type of homogeneous catalyst commonly used in oxidative desulfurization. Related literatures about heteropolyacid catalysis are numerous. F. M. Collins *et al.*<sup>48</sup> used phosphotungstic acid as catalyst and tetraoctylammonium bromide as phase transfer agent to treat diesel, founding that all sulfur-containing compounds could be oxidized and the highly substituted dibenzothiophenes which containing a thiophene nucleus were easier to be oxidized. D. Huang *et al.*<sup>71</sup> showed that a complete DBT conversion with its concentration of 3000 ppm can be shortened to 10 min at 70 °C when using octadecyltrimethylammonium bromide (STAB) as phase transfer agent in  $\text{H}_2\text{O}_2$ /phosphotungstic acid system. K. Yazu *et al.*<sup>39</sup> proved that 4,6-DMDBT, the most refractory sulfur-containing compound in HDS, can be oxidized with  $\text{H}_2\text{O}_2$ /12-phosphotungstic acid as catalyst in *n*-octane/acetonitrile biphasic system.

Researchers found that the decomposition of  $\text{H}_2\text{O}_2$  competed with the catalytic oxidation of DBT. Therefore, the main cost involved in treating fuel oils by above-mentioned catalytic oxidative desulfurization systems is the huge amounts of  $\text{H}_2\text{O}_2$  consumption. Maybe this oxidative desulfurization process can be a complement for conventional HDS process. Researchers also demonstrated that complex intermediates would form with heteropolyacid as catalyst while peroxy acid would form with formic or acetic acid as catalyst (Fig. 3).

## 2.2. Heterogeneous catalysts using different carriers

Heterogeneous catalysts have become the research focus for the solid catalysts bridge the catalysts separation gap. And the catalytic activity that really matters is the solid active components, which are usually precious metals or rare-earth metals, such as nickel, iridium, tungsten, palladium, cobalt, scandium, yttrium and lanthanum *etc.* But little attentions and studies are given to these single solid active components due to the following common flaws: unequally distributed components,

low mechanical strength and weak thermal conductivity. Consequently, these active metals are unstable and losing activity easily in catalytic reaction for they are susceptible to external conditions. To solve the above-mentioned problem and achieve the ultra-desulfurization requirements, numerous studies have been done and confirmed that deposition of active metals on suitable supports is an important one.

### 2.2.1. Metal oxide as the carrier

**2.2.1.1.  $\text{Al}_2\text{O}_3$  as the carrier.**  $\text{Al}_2\text{O}_3$  as an atomic crystal with a surface area below  $200 \text{ m}^2 \text{ g}^{-1}$  is easy to shape into a fixed shape which can resist high temperature and withstand wear and tear, so it has attracted numbers of researchers' attention. The performance of removing S-containing compounds with this metal oxide and the preparation of the catalysts by different methods have been studied. The similar reaction mechanism by un-promoted and promoted catalysts could be obtained in previous studies.

A series of  $\text{Mo}/\text{Al}_2\text{O}_3$  catalysts with various Mo contents were prepared and tested for the oxidation of sulfur compounds using *tert*-butyl hydroperoxide (*t*-BuOOH) as the oxidant in kerosene. There was remarkable (beneficial or otherwise) on the oxidation activity of DBT seen from Fig. 4, the loading amounts

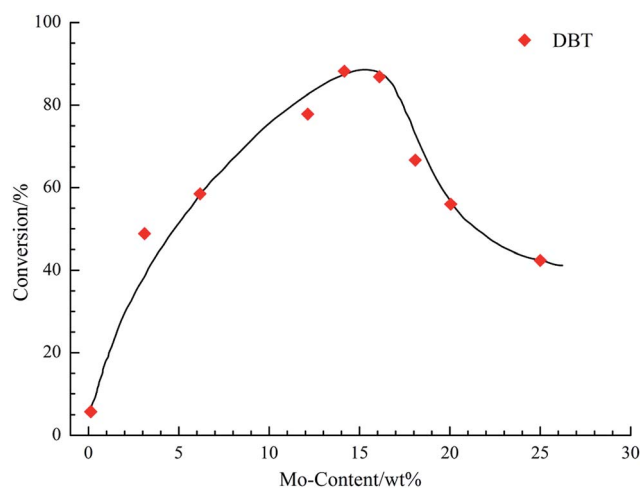


Fig. 4 Oxidation activities of DBT in kerosene on  $\text{Mo}/\text{Al}_2\text{O}_3$  catalysts with various Mo contents at 110 °C.<sup>72</sup>

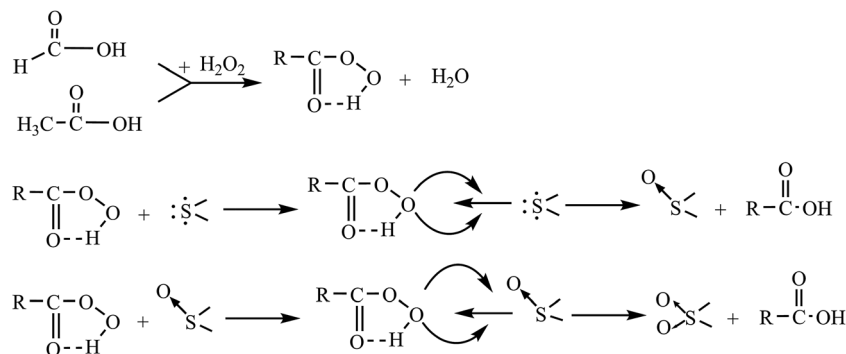


Fig. 3 Oxidation steps in  $\text{H}_2\text{O}_2$ -formic/acetic acid system. R represents hydrogen group in  $\text{H}_2\text{O}_2$ /formic acid system and represents methyl group in  $\text{H}_2\text{O}_2$ /acetic acid system, the symbol containing "S" represents model sulfur compound in oils.

of Mo ranging from 10 wt% to 15 wt% were perceived as the optimal content for this reaction, however, the very low oxidation activity was observed when too little or too much Mo were dispersed on  $\text{Al}_2\text{O}_3$ . It was attributed to insufficient active sites were supplied when Mo concentration was too low, and accumulation of Mo oxides were happened on catalyst surface when Mo concentration was too high.<sup>72</sup> Wan NWA *et al.*<sup>73</sup> investigated the catalyst of  $\text{Fe}/\text{MoO}_3\text{-PO}_4/\text{Al}_2\text{O}_3$  calcined at 500 °C, almost 96% sulfur was transformed to sulfone in commercial diesel. Jeyagowry *et al.*<sup>66</sup> prepared  $\gamma\text{-Al}_2\text{O}_3$  supported manganese and cobalt oxide by an incipient wetness method to study the oxidation of the sulfur impurities by air in diesel. The catalysts prepared by this method were highly effective for the selective oxidation of S-containing compounds with sulfur level can be easily reduced to as low as 40–60 ppm. Luis<sup>74</sup> researched a series of  $\text{V}_2\text{O}_5$  metal oxides supported on different carriers, founding that the oxidation activity of DBTs largely depends on the support used following the next order: alumina > titania > niobia > Al-Ti mixed oxide > SBA-15. A strong boosting effect on sulfone conversion was recorded when vanadia was added to the supports. Luis also found that the feed concentration of N-compounds had a significant influence on sulfone conversion, which might because the nitrogen compounds could occupy the adsorption sites of  $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$  catalyst.

**2.2.1.2.  $\text{SiO}_2$  as the carrier.** Silica has stable physical and chemical properties, it is a high surface area support with controlled pore size.<sup>75,76</sup> Silica supported Mo, W and V-based catalysts are the most prevalent commercial catalysts which exhibit excellent activity, but they are easy to sinter and agglomerate. Maybe this shortcoming could be made up for by modifying related carriers and catalysts.

Prasad *et al.*<sup>77</sup> modified the  $\text{MoO}_3/\text{Al}_2\text{O}_3\text{-SiO}_2$  catalysts by Bi, and these combination metal oxide catalysts exhibited not only high catalytic activities but also high stability in the oxidation of 4,6-DMDBT. According to other researches, addition of Ca and Ba in  $\text{MoO}_3/\text{SiO}_2$  catalysts could efficiently improving the dispersion of  $\text{MoO}_3$  on support and thus improving the performance of sulfur removal. Bazyari *et al.*<sup>78</sup> prepared amorphous microporous  $\text{TiO}_2\text{-SiO}_2$  nanocomposites by sol-gel method. Under the optimal circumstances, the efficiency of sulfur removal could exceed 98% after 20 min. It was found that the amount of titanium in the microporous  $\text{TiO}_2\text{-SiO}_2$  catalysts had significant effects on the catalytic oxidation activity. The efficiency increased from 54% to 98% by raising the reaction temperature from 323 K to 353 K. At the same time, a series of P modified  $\text{MoO}_3/\text{SiO}_2$  catalysts revealed that sulfur conversion could be improved from 47.3% to 92.6% at 50 °C.<sup>79</sup> Fraile *et al.*<sup>80</sup> prepared the catalyst of  $\text{Ti}/\text{SiO}_2$  by grafting method with aqueous  $\text{H}_2\text{O}_2$  as oxidizing agent, removing sulfur by oxidation under different parameters, such as catalyst amounts, sulfur concentration, O/S molar ratio and oxidant adding methods. Results suggested that the number of Ti sites could be optimized by tuning the silanization conditions of the catalysts. Caero *et al.*<sup>74</sup> found that the lower oxidation activity on  $\text{SiO}_2$  support attributed to the lower polarity of V–O bond on  $\text{SiO}_2$  compared to  $\text{Al}_2\text{O}_3$ . Chang *et al.*<sup>65</sup> observed that a dramatic improvement was achieved through the addition of Ca when

$\text{MoO}_3/\text{SiO}_2$  was used as catalyst. The idea of using alkaline earth metals to modify supports may open a new way to remove sulfur from oils Zhang *et al.*<sup>81</sup> confirmed this point, and indicated that DBT could almost be removed completely under atmospheric pressure and a reaction temperature as low as 50 °C.

Different methods can produce different catalysts that have different performances on catalytic activity and sulfur removal efficiency. Chang *et al.*<sup>65</sup> reported that the optimal preparation condition of  $\text{MoO}_3/\text{SiO}_2$  was the 0.05 Ca/Mo molar ratio with WHSV 30  $\text{h}^{-1}$ . Moreover,  $\text{MoO}_3/\text{SiO}_2$  modified with P could exhibit extremely high activity in desulfurization reaction, data showed that 92.6% DBT conversions were obtained at atmospheric pressure, 50 °C. The silica support-based catalysts can be prepared by sol-gel and impregnation methods. Xun *et al.*<sup>82</sup> prepared the catalyst of  $\text{SiO}_2$  supported  $\text{SiW}_{12}\text{O}_{40}$ -based ionic liquid (SiW-IL) by sol-gel method, the removal rate of dibenzothiophene (DBT) with this supported catalyst reached 99.9%. Through the incipient wetness impregnation method, the catalyst of  $\text{MoP}_{1.0}/\text{SiO}_2$  was prepared and could achieve 92.6% DBT removal. Li *et al.*<sup>83</sup> successfully synthesized  $[\text{C}_4\text{mim}]_3\text{-PW}_{12}\text{O}_{40}/\text{SiO}_2$  catalyst by a facile hydrothermal process and the best performance could reach 100% DBT removal. Therefore, it can be seen that sol-gel and hydrothermal methods present slight advantages over IWI method.

### 2.2.2. Molecular sieve as the carrier

**2.2.2.1. Mesoporous silicates as the carrier.** There are different types of mesoporous silicates which have been widely used because of their good thermostability, high surface area, large pore volume, uniform pore size and regular structure. However, the industrialization of the homogeneous silica MCM-41 mesoporous molecular sieves was limited for the defects including poor heat endurance, weak surface acidity and low catalytic activity. And the incorporation of various heteroatoms into the framework can effectively overcome some disadvantages and improve catalytic oxidation activity.

Li *et al.*<sup>84</sup> verified that the Fe–MCM-41-based catalysts were very promising for the desulfurization reaction with  $\text{H}_2\text{O}_2$ . Especially, the optimal catalyst activity could be achieved with the iron content at 11.75%. The first time of using Ti–MCM-41 catalyst to catalyze the desulfurization of DBT and its derivatives was in 1996.<sup>85</sup> Antonio Chica *et al.*<sup>64</sup> researched the Ti–MCM-41 catalyst on which Ti acted as the additive to improve its desulfurization activity and durability in ODS of transportation fuels. The author pointed out that the removal of sulfur with Ti–MCM-41S catalyst could be improved by calcination, compared to that with CoAPO-5 catalyst or Ti-Beta catalyst. Other catalysts have been researched as well. For instance, D. Nedumaran *et al.*<sup>86</sup> used hydrothermal sol-gel method to synthesize Si–Sn–MCM-41 (molar ratio of Si/Sn: 110) mesoporous molecular sieve, which exhibited high catalytic activity at 325 °C. Xie *et al.*<sup>87</sup> used impregnation method to prepare the  $\text{MCM-41}/\text{Q}_4\text{-H}_2\text{Se}^{\text{IV}}_3\text{W}_6$  and  $\text{MCM-41-NH}_2/\text{Q}_4\text{-H}_2\text{Se}^{\text{IV}}_3\text{W}_6$  and the research team showed that the mesoporous material was not the decisive factor in determining catalytic activity. The available data indicated that the inactivation of some active sites might be the cause for the low catalytic activity of  $\text{MCM-41}/\text{Q}_4\text{-H}_2\text{Se}^{\text{IV}}_3\text{W}_6$  catalyst. MCM-41 modified with cesium oxide have been developed by Hyeonjoo

Kim *et al.*<sup>88</sup> The results displayed that Cs was located inside the pores of MCM-41 and also indicated that the maximum number of basic sites were obtained in Cs (3 wt%)/MCM-41 catalyst, which agrees with the basicity enhancement of MCM-41 when cesium act as additive.

**2.2.2.2. SBA as the carrier.** SBA is a mesoporous molecular sieve composed of SiO<sub>2</sub> and has no intrinsic catalytic activity. However, special attention should be paid to this material due to its high porosity, large specific surface area, ordered hexagonally mesopores and good mechanical stability.<sup>89,90</sup> So surface modification of this kind of molecular sieve by adding transition metal oxide is of great interest. SBA can be used as carrier and adsorbent, has exchangeable cations and sufficient acid centers (with Brönsted acid) on the surface. Now the study application focuses on the utilization of its surface acidity. And incorporation of various kinds of impurity atoms can be used to regulate the amount of acid and the surface acidity. Various transition metals were introduced into SBA support and these modified SBA-based catalyst had been studied, which demonstrated that titanium could improve the activity and life of the molecular sieve support with great potential for industrial application. Shi *et al.*<sup>91</sup> showed that hierarchically porous Ti-SBA-2 with 5 wt% Ti exhibited excellent performance in desulfurizing diesel fuel at low temperature (40 °C and 25 °C). Kim *et al.*<sup>92</sup> studied the effect of Ti content in SBA-15 on sulfur selective catalytic oxidation. The synthesis procedure affected the dispersion of the 4-coordinate titanium tetrahedral Ti<sup>4+</sup> specie. Besides, the content of active sites and the size of mesopore also would affect the activities of various Ti-modified SBA-15 catalysts. Although SBA-15 is a potential support to be modified in removing sulfur, it needs further attention in terms of synthesis procedure, synthesis cost and reasonable modification which includes tunable mesopore size, high stability and ordered arrangement.

In conclusion, many researches have comprehensively explored the carriers and these modified catalysts could achieve high sulfur conversion. But it needs more intensive exploration for industrial applications.<sup>93,94</sup> Hydroperoxide, as the main oxidizing agent, has been researched utilizing different kinds of catalysts. Zhuang *et al.*<sup>95</sup> suggested that the initial step was extraction of DBT into the acid sites with the presence of H<sub>2</sub>O<sub>2</sub>, and subsequently it further reacted with polyoxoperoxo species to form according sulfone. Thus the number of acid sites is significant in catalytic activity of catalysts. It is known that the pure SBA-15 exhibits specific bands at approximately 799 and 1083 cm<sup>-1</sup>. And many researchers<sup>59,96,97</sup> studied the variation caused by the introduction of impure atoms.

Sum up the analysis above, the homogeneous catalysts can offer high yields attribute to their uniform active center and independent molecular or ion, and without the problem of surface heterogeneity and internal diffusion on solid catalysts. Thus homogeneous catalysts allow highly selective conversion of substrates at mild reaction conditions, which have received much attention and have already acquired some achievements. However, homogeneous systems are always regarded as ill-defined with many problems, including easy decomposition and deactivation, and separation problem as well, which

determine the economic feasibility of production processes. On the other hand, heterogeneous systems may light up the catalysis area with sparkling rewards as catalyst recovery from the homogeneous systems is typically stropopy. The properties of high pore volumes, high specific surface areas, and narrow pore size distributions can allow support deposit and stabilize active components, which opens up new reaction pathways for the catalysis industry. Numerous efforts have been made to incorporate homogeneous catalysts or active metals on solid supports, such as active carbon, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub>, mesoporous silicates, and SBA *etc.*

### 3. Effects of reaction conditions

With the deepening of the study, the catalysts with high stability and selectivity, good activity and broad range of operating temperature have achieved great progress. However, there is still a oxidation question regarding catalyst deactivation.

#### 3.1. Effects of active components

Active component is one of the main ingredients to catalyze sulfur in flue oils and loss of it often leads to catalyst deactivation. Often during the oxidation reaction, the catalysts activity would be affected by the active component leaching. It causes a decline in activity for both supported metal oxide catalysts<sup>98</sup> and supported heteropolyacid catalysts.<sup>99</sup> The effects of active component can be divided into two results, irreversible and reversible. It is reversible when sulfone adsorption occurred on catalysts surface, and this effect will disappear with solvent extraction. However, the dissolution of active component at prophase will result in an irreversible deactivation of the catalysts.<sup>99</sup>

Wang *et al.*<sup>100</sup> studied the deactivation and regeneration of PW<sub>12</sub>/HMS catalyst (Fig. 5). The results indicated that the PW<sub>12</sub> active species would partially leach into solvent in every cycle.

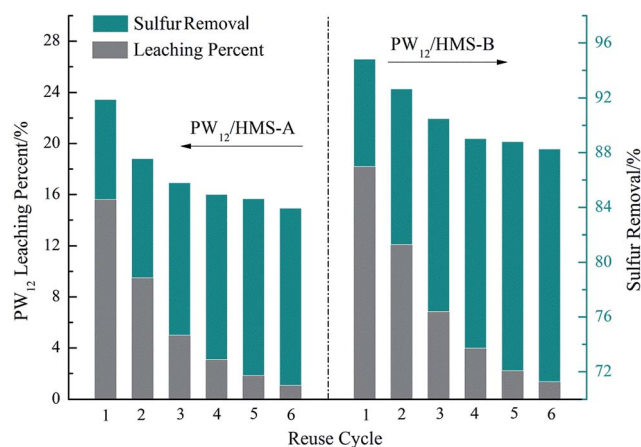


Fig. 5 Sulfur removal and the leaching percent of PW<sub>12</sub> along with the repetition of dissolving experiment. Dissolution experiment conditions: catalyst dosage 0.3 g,  $T = 60\text{ }^{\circ}\text{C}$ ,  $t = 60\text{ min}$ , water 100 mL. ODS conditions: catalyst dosage 0.3 g, H<sub>2</sub>O<sub>2</sub>/S = 8 : 1 (molar ratio),  $T = 60\text{ }^{\circ}\text{C}$ ,  $t = 60\text{ min}$ , pre-oxidation time 6 min, model fuel and acetonitrile 20 mL.<sup>100</sup>

And the conversion of BT exhibited a downward trend with the leaching of  $PW_{12}$ . The reason for this might be that the continuous dissolution of the active species from the catalysts would lead to the reduction of active sites. The experiment also revealed that the effect of the catalyst preparation method was great, for instance, the ultrasonic impregnation might cause more grievous dissolution of  $PW_{12}$  species. However, the deactivation of catalyst might not just attributed to the leaching of active components, combined actions such as pore blocking, adsorption of products and impurities on surface area would be other reasons for catalyst poisoning.

### 3.2. Effects of N-containing compounds

The S-containing compounds in many kinds of fuel oils are coexisting with N-containing compounds, which would gather on the catalyst surface or selectively react with the active matters in the catalyst and then occupy the active sites during the long time contact with catalyst. In the study of traditional supported catalyst, a small amount of N-containing compounds can have a great effect on the activity of the catalyst. Ishihara *et al.*<sup>63</sup> studied the influence of indole, quinoline, acridine and carbazole on catalytic activity of the catalysts, indicating that the ODS activity decreased most in the presence of indole than in the presence of other nitrogen compounds and the influence rank was indole > quinoline > acridine > carbazole. Other researchers also studied the effects of N-containing compounds for sulfur removal (Table 2). It can be seen that the sulfur removal rate was affected severely in presence of the N-containing compounds. L. C. Caero *et al.*<sup>101</sup> suggested that the nitriles which form in the process of oxidizing different kinds of fuel oils would accumulate on the catalyst surface, then reacted with catalyst and thus causing activity loss. Similar results were also obtained by Y. H. Jia *et al.*<sup>102</sup> Previous studies showed that these nitrogen compounds could occupy the acid sites of catalysts, and affect the catalytic efficiency.<sup>103–105</sup> Maybe the extraction solvent or adsorbent to remove N-containing compounds and

regeneration of catalysts are better solutions. Kim *et al.*<sup>106</sup> studied the removal of N-containing compounds by three typical adsorbents (activated alumina, activated carbon and nickel-based adsorbent) and got an ideal result. X. Chen *et al.*<sup>109</sup> reported that dilution with water followed by simple distillation could reverse the catalyst deactivation caused by N-containing compounds. And high temperature calcination and solvent extraction were the most common methods for regenerating catalysts that applied in ODS process.

The N-containing compounds are categorized into two types: (1) basic nitrogen-containing compounds, *i.e.*, quinoline, aniline, pyridine, and their derivatives; (2) non-basic compounds, *i.e.*, carbazole, pyrrole, indole, and their derivatives.<sup>110</sup> Besides the competitive adsorption between sulfur and nitrogen compounds on the adsorption sites, the basic character of N-compounds will also influence the catalysts activity. Hence, the specific toxic effect of quinoline sometimes was more significant than indole.<sup>101</sup> Researcher<sup>101</sup> attributed a stronger poisoning effect caused by quinoline to its 6-membered ring.

### 3.3. Effects of reaction temperatures

Temperature is an important factor influencing catalysts activity, thus, the effects of temperature on oxidative desulfurization were studied by many researchers. As shown in Table 3, the removal rate is subject to the reaction temperature.

Temperature rising within a certain range will improve catalyst activity and sulfur removal rate, therefore, increasing the reaction temperature properly is beneficial for desulfurization reaction.<sup>111</sup> Higher temperature not only can accelerate the oxidation rate, but also can promote the desorption of sulfone from the active sites of catalyst. Sulfone would strongly adsorbed on the surface of catalyst at low temperature, which would prevent further adsorption of S-containing compounds to be oxidized and result in low conversion of sulfur compounds. However, it can also be seen that the sulfur conversion rate decreased when the reaction temperature exceeds the optimal temperature.

Table 2 Total sulfur removal rate of S-compound

S-compound	Reaction time/min	With quinoline	With carbazole	With indole	Ref.
		S removal/%	S removal/%	S removal/%	
BT	60	73.8	87.2	87.8	101
DBT	60	97.0	99.0	98.2	
4-MDBT	60	77.0	97.0	96.0	
4,6-DMDBT	60	59.0	90.0	89.0	
Thiophene	360	94.3	—	93	102
BT	30	82.1	90.4	83.5	
BT	90	100	100	100	107
4,6-DMDBT	360	85.7	—	82.5	
BT	180	48.9	65.5	17.7	
DBT	180	98.7	100	62.5	
4-MDBT	180	93.9	98.1	47.5	108
4,6-DMDBT	180	83.2	92.8	35.4	
Model oil	DBT	300	—	30.0	
	BT	300			
	Th	300			



Table 3 Effects of temperature on substrate removal using different catalysts

Catalysts	Oxidants	Substrates	Temperature range/°C	Optimal temperature/°C	Removal rate/%	Ref.
TiO <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	DBT	313–343	343	70.0–100	112
SEP-1	H <sub>2</sub> O <sub>2</sub>	DBT	45.0–60.0	60.0	72.5–99.4	113
SIM41C	TBHP	DBT	313–393	353	49.1–98.4	111
TiO <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	DBT	30.0–60.0	40.0	64.2–99.1	114
HPW/AC	H <sub>2</sub> O <sub>2</sub>	Thiophene	70.0–90.0	90.0	80.7–90.0	115
Fe–TiO <sub>2</sub> -0	H <sub>2</sub> O <sub>2</sub>	DBT	30.0–80.0	80.0	21.7–54.0	116
Fe–TiO <sub>2</sub> -1	H <sub>2</sub> O <sub>2</sub>	DBT	30.0–80.0	80.0	30.8–76.5	116
Fe–TiO <sub>2</sub> -3	H <sub>2</sub> O <sub>2</sub>	DBT	30.0–80.0	80.0	41.4–81.5	116
Fe–TiO <sub>2</sub> -5	H <sub>2</sub> O <sub>2</sub>	DBT	30.0–80.0	80.0	70.2–99.6	116
Fe–TiO <sub>2</sub> -10	H <sub>2</sub> O <sub>2</sub>	DBT	30.0–80.0	80.0	80.5–100	116

Too high temperature would cause catalyst agglomeration and sintering, which may greatly affect the contact between DBTs and the active sites. Besides, excessive temperature would also result in the low thermostability of TBHP and the decomposition of H<sub>2</sub>O<sub>2</sub>. So the best performance with different catalysts system can only be obtained under the optimal reaction temperature. Moreover, U. Arellano *et al.*<sup>116</sup> studied the effect of reaction temperature for DBT oxidation with a series of Fe–TiO<sub>2</sub> catalysts. The results showed that the performance improved with increasing temperature, however, even under the optimal temperature, the pure TiO<sub>2</sub> exhibited relatively low catalytic activity in DBT oxidation, which revealed that the catalyst activities were affected by combined actions. Our research group<sup>117–119</sup> studied the efficiency of sulfur removal with oil-soluble oxidant under different temperatures, indicating that in a certain range of temperature, the movement of molecular would be speeded up with an increase of temperature, however, when the temperature was above some kind of range, model oil lost due to gasification and volatilization. They also found CYHPO oxidant would decompose at high temperature.<sup>119–121</sup> These findings are very valuable for future industrial applications. Hence, selecting proper reaction temperature is significant to the removal of sulfur compounds.

In addition to the factors discussed above, other factors such as the generation of low active compounds, the embedding of active components and the volatilization of active components would also lead to catalysts deactivation.

In conclusion, many reaction parameters would affect the catalytic activity of catalysts, thus affecting the sulfur removal efficiencies. Additionally, the effects of ODS on achieving ultra-clean oils are equally deserving of attention. Previous results suggested that the process of ODS were composed of oxidation and extraction, total sulfur removal depends on the contribution of oxidation and extraction steps. Therefore, types of oxidant, composition of oils and properties of polar solvent would also exert effects on desulfurization efficiency. For this reason, it is significant to further study the contribution of each factor, in order to better understand the real activity of the catalyst. Except for above factors mentioned, studies on reaction time, O/S molar ration and catalyst amount are necessary for the purpose of determining the optimal reaction conditions for every single catalysis system.

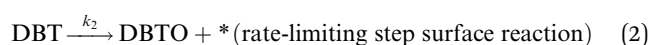
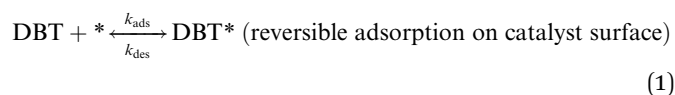
## 4. Kinetics

Lots of works had been done for studying the kinetics and mechanism of removing the sulfur over different kinds of catalysts. The research of kinetics for ODS over different catalysts was based on power-law kinetics equations and obtained from related mechanistic analysis or both of them.

### 4.1. Kinetics model of ODS

The research about the rate of reaction *vs.* oxidant was not sufficient, because in most cases, catalytic oxidation reaction is performed with an excess of oxidant (*i.e.* H<sub>2</sub>O<sub>2</sub>, TBHP, or light). It is believed that the reaction kinetic is of the zeroth order on oxidant amounts. L. Kong *et al.*<sup>122</sup> proved that the reaction order of H<sub>2</sub>O<sub>2</sub> was zero by plotting reaction rate constant against the concentrations of H<sub>2</sub>O<sub>2</sub>. Decades of researches have shown that reactions of catalytic oxidation of sulfur compounds presenting in oils are of the first or quasi-first order of sulfur compounds.<sup>38,95,123–131</sup> The quasi-first order kinetics is frequently observed in quite a set of photodesulfurization systems, in both “solid–binary immiscible liquid” and “solid–liquid” systems, for regular single site photocatalysts, TiO<sub>2</sub>-based photocatalysts and photocatalytic nanoporous thin films. In minor cases, chemical reaction is of the zeroth order on the sulfur compound. This situation is observed when fuel oils contain high concentrations of sulfur compounds.<sup>132</sup> Therefore, it can be assumed that chemical reaction is, in most situations, of the first order on sulfur compounds. The first or quasi-first order of chemical reaction is in line with the Langmuir–Hinshelwood mechanism of homogeneous and heterogeneous catalytic reactions.

M. Chamack *et al.*<sup>96</sup> studied the kinetics of ODS reaction in depth over platelet mesoporous silica loaded with Cs<sub>x</sub>H<sub>3–x</sub>[PMO<sub>12–y</sub>W<sub>y</sub>O<sub>40</sub>] ( $x = 1–3, y = 2–10$ ). The results showed that the rate limiting step was the oxidation process of DBT to DBTO<sub>2</sub>. Supposed that the heat- and mass-transfer limitations were negligible, the surface reaction occurred as follows:



where \* refers to activated surface site that adsorbs DBT and produces DBT\*, and  $k_2$ ,  $k_{des}$ ,  $k_{ads}$  correspond to the rate constants for surface reaction, desorption and adsorption, respectively. The eqn (1) shows that the adsorption of DBT onto the solid catalyst is reversible, then the resulting DBT\* is converted to DBTO in a rate-limiting step. Considering the Langmuir–Hinshelwood mechanism, the reaction rate ( $r$ ) could be expressed as:

$$r = k_2[\text{DBT}^*] \quad (3)$$

Through the steady-state approximation, the concentration of activated intermediate is in accord with the following equation:

$$[\text{DBT}^*] = k_{ads}[\text{DBT}][^*]/(k_{des} + k_2) \quad (4)$$

If the rate constant is defined as:

$$[k] = k_2 k_{ads} [^*]/(k_{des} + k_2) \quad (5)$$

The form of rate equation is equal to the following expression:

$$r = k[\text{DBT}] \quad (6)$$

which reveals that the reaction is a pseudo-first-order reaction with respect to DBT. Hence, if the concentration of DBT at  $t = 0$  and  $t = t$  can be expressed as  $[\text{DBT}]_0$  and  $[\text{DBT}]_t$ , the reaction rate constant ( $k$ ) can be expressed by the integrated first-rate law:

$$\ln([\text{DBT}]_t/[\text{DBT}]_0) = -kt \quad (7)$$

To evaluate the kinetic of DBT oxidation reaction, the  $\ln([\text{DBT}]_t/[\text{DBT}]_0)$  were plotted as the function of time. The obtained regression values were exceeded 0.9, which showed that the kinetic data were well fitted to pseudo-first-order kinetic rates. According to Langmuir–Hinshelwood mechanism about catalytic reaction, these results were in agreement with mentioned assumptions. Other experiments<sup>133–135</sup> have the same results, and the activation energy for the sulfur compounds oxidation can be obtained by the use of the Arrhenius equation (eqn (8)).

$$\ln k = \ln A - E_a/RT \quad (8)$$

where  $A$ ,  $E_a$ ,  $R$  and  $T$  are the pre-exponential factor, the activation energy ( $\text{kJ mol}^{-1}$ ), universal gas constant ( $8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$ ) and temperature, respectively. The kinetic parameters obtained by various researchers are listed in Table 4.

From Table 4 we can concluded that the oxidation reaction of sulfur compounds is strongly temperature dependent, and the reaction rate constant ( $k$ ) may be different for the same substrate under different desulfurization systems. The catalytic activity order of the sulfur compounds is consistent with the apparent rate constant order. Researchers also proved that the apparent rate constant was greatly affected by the catalyst/oil mass ratios. As a consequence, it is assumed that the rate-

limiting process might be controlled by the mass transfer of a reactant across the diffusion layer next to the interface.

#### 4.2. Kinetics model of catalysts deactivation

Catalyst deactivation is another important aspect that can not ignored during the oxidation process. Many researchers also studied the kinetics of catalyst deactivation.<sup>137,138</sup> B. Saha *et al.*<sup>137</sup> investigated the kinetics of catalyst deactivation over TS-1 catalyst, they found that the reaction rates became constant after around 60 min. This proved that the catalyst became deactivated after certain period of reaction. Supposed that the deactivation of catalyst was independent deactivation, the catalyst deactivation rate equation can be represented as:

$$-dC_A/dt = (W/v)(-r_A) = (W/a)k' C_A a \quad (9)$$

and,

$$-da/dt = k_d a \quad (10)$$

where  $k'$  and  $k_d$  is the rate constant of the reaction and deactivation, respectively;  $W$  and  $a$  is the catalyst weight and activity, respectively.

Considering unit initial activity of the catalyst ( $a_0 = 1$ ), integration of eqn (10):

$$a = a_0 \exp(-k_d t) \text{ and } a = \exp(-k_d t) \quad (11)$$

From eqn (10) and (11),

$$-dC_A = (W/a)k' C_A \exp(-k_d t) \quad (12)$$

After separation and integration of eqn (12),

$$\ln(C_{A_0}/C_A) = (Wk'/vk_d)(1 - \exp(-k_d t)) \quad (13)$$

It is clear from eqn (13) that the substrate concentration for an irreversible reaction followed a decreasing trend with the gradual deactivation of the catalyst and with the progress of the reaction but never became zero even after infinite time. Therefore, the equation can also be written in the following manner:

$$\ln(C_{A_0}/C_{A_\infty}) = Wk'/(vk_d) \quad (14)$$

where  $C_{A_0}$  and  $C_{A_\infty}$  correspond to the concentration of the substrate at  $t = 0$  and  $t = 1$ , respectively. Hence, combining eqn (13) and (14):

$$\ln[\ln(C_{A_0}/C_{A_\infty})] = Wk'/(vk_d) \quad (15)$$

By plotting the  $\ln[\ln(C_{A_0}/C_A)]$  versus  $t$  at different temperatures, the apparent reaction rate constants and the deactivation rate constants could be calculated from the intercept and slope of the plot. The highest rate constant of the reaction and deactivation respectively was 0.65 and 0.011 at 70 °C, and the activation energy of thiophene was calculated to be 19.13  $\text{KJ mol}^{-1}$ .

In conclusion, the kinetics of oxidation reaction and deactivation process are basically follow the pseudo-first-

Table 4 Reaction rate constant of different desulfurization system

Catalyst	Reactants	Reaction temperature/°C	Rate constant/min <sup>-1</sup>	Correlation factor (R <sup>2</sup> )	Activation energy/kJ mol <sup>-1</sup>	Ref.
SPIL	4,6-DMDBT	60.0	0.02258	0.9969	54.2	131
SPIL	BT	60.0	0.00798	0.9922	65.3	131
NaPW	BT	70.0	0.16520	0.9953	57.8	133
NaPW	DBT	70.0	0.38020	0.9978	29.9	133
PW	BT	70.0	0.14350	0.9971	63.6	133
PW	DBT	70.0	0.35850	0.9977	45.1	133
PMo	BT	70.0	0.02300	0.9938	38.2	133
PMo	DBT	70.0	0.05200	0.9971	28.2	133
SiW	BT	70.0	0.00630	0.9913	36.7	133
SiW	DBT	70.0	0.00900	0.9963	27.6	133
Cs <sub>2</sub> Mo <sub>8</sub> W <sub>4</sub> /SBA	DBT	60.0	0.12070	0.9790	—	96
[C <sub>4</sub> <sup>3</sup> MPy]FeCl <sub>4</sub>	DBT	25.0	0.99510	0.9938	—	136
TS-1	Th	60.0	0.02274	0.9970	29.9	122
H <sub>5</sub> PMo <sub>10</sub> V <sub>2</sub> O <sub>40</sub>	DBT	60.0	0.04440	0.9950	—	95
H <sub>5</sub> PMo <sub>10</sub> V <sub>2</sub> O <sub>40</sub>	BT	60.0	0.02430	0.9980	—	95
H <sub>5</sub> PMo <sub>10</sub> V <sub>2</sub> O <sub>40</sub>	Th	60.0	0.01320	0.9970	—	95

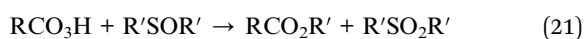
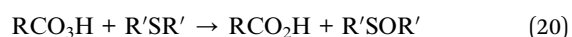
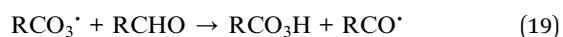
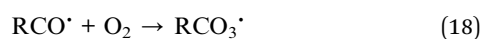
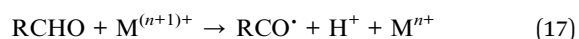
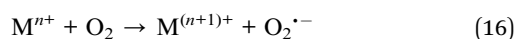
order equation, and the reaction rate constant ( $k$ ) is affected by many factors, such as substrate, catalyst and temperature *etc.* The related reaction mechanism and kinetics may help us shed light on specific desulfurization process, vital rate-controlling step and inevitable catalyst deactivation. Therefore, further intensive investigations should be done on this point.

## 5. ODS mechanism with different oxidant

At present, many catalysts have been studied, but most of them lack sufficient clear knowledge of the ODS reaction mechanism. In this review, the development progress of the reaction mechanism which removed sulfur by different oxidizing agents was summarized.

### 5.1. O<sub>2</sub> as the oxidant

Some researchers used O<sub>2</sub> as the oxidizing agent to remove sulfur in ODS,<sup>139–141</sup> which could get a high sulfur conversion rate. The effect of O<sub>2</sub> is to form peroxy group and donate oxygen atom, which promotes the formation of sulfone. The mechanism is as follows:<sup>141</sup>



where M<sup>(n+1)+</sup> and Mn<sup>+</sup> represent a metal ion, R is aryl or alkyl group, R'SR' represents sulfides, R'SOR' represents sulfoxides, and R'SO<sub>2</sub>R' is sulfones.

### 5.2. *tert*-Butyl hydroperoxide as the oxidant

The mechanism of *tert*-butyl hydroperoxide (TBHP) as the oxidizing agent has also been studied, because of the cost-effectiveness and practicability. High sulfur removal efficiency can be achieved using TBHP oxidant and heterogeneous catalysts. Complex species<sup>142</sup> or metal-peroxide intermediate<sup>100</sup> formed with the nucleophilic attack of TBHP on catalysts surface. Due to the effect of the catalysts of Co/Mn/Al<sub>2</sub>O<sub>3</sub>, the first step is the formation of MnO<sub>2</sub> (Mn<sup>4+</sup>) and Co<sub>3</sub>O<sub>4</sub> (Co<sup>4+</sup>) at low calcination temperature, then these complex species will undergo the nucleophilic attack of divalent sulfur of DBT to form dibenzothiophenesulfoxide(III) and *tert*-butanol(IV), and dibenzothiophenesulfoxide(III) will finally become dibenzothiophenesulfones(V) *via* the oxidation of complex species.<sup>100</sup> At present, the TBHP used as the oxidizing agent to remove sulfur mainly follows the nucleophilic reaction mechanism.

W. N. W. Abdullah *et al.*<sup>73</sup> analyzed the mechanism using Fe/MoO<sub>3</sub>-PO<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> and TBHP as the catalyst and oxidizing agent respectively. Firstly, the *tert*-butyl hydroperoxide conducted the nucleophilic attack on Mo=O to form peroxometallic complex, then the obtained species on the surface of the catalyst reacted with sulfur in the DBT. In the process of reaction, DBT sulfoxide and polymolybdate species were formed, and sulfoxide would undergo further oxidation quickly to generate DBT sulfone. The results suggested that the addition of Fe dopant could promote the formation of active intermediate. W. A. W. A. Bakar *et al.*<sup>143</sup> studied the mechanism of ODS with WO<sub>3</sub>/MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> as the catalyst (Fig. 6). The detailed reaction process between organic sulfur compounds and TBHP was explained, but it was not clear about the rate controlling steps in reaction.

D. H. Wang *et al.*<sup>111</sup> researched the ordered mesoporous silica catalysts with structures of MCM-41, MCM-48 and SBA-15 for sulfur removal. The TBHP was firstly adsorbed on the

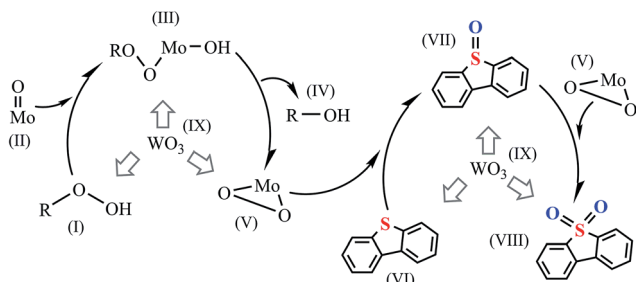


Fig. 6 Proposed mechanism for the oxidation of dibenzothiophene by the  $\text{WO}_3/\text{MoO}_3/\text{Al}_2\text{O}_3$ .<sup>145</sup>

surface of catalysts to form a five member-ring *via* reciprocal hydrogen bonding. And dibenzothiophene sulfoxide was formed by the sulfur atom attacking the oxygen atom in the five-member ring. Then the formed sulfoxide could be adsorbed at the active sites of silanol radicals by hydrogen bond. Finally, the species would react with the oxygen atom of unbound TBHP to form sulfone, which can be easily flowed down by extraction solvent. The author pointed out that the generation of dibenzothiophene sulfoxide controlled the reaction rate. Moreover, Kropp *et al.*<sup>144</sup> did the similar related study and found that a reversal was existed in mechanism, from electrophilic reaction to nucleophilic reaction, when sulfide is oxidized to sulfoxide.

In practice, ODS catalysts are composed of many kinds of porous materials. It is necessary to further test and analyze the oxidation performances with different TBHP-catalyst systems in the laboratory. Various positive effects or negative effects would happen with supports or inhibitors during the catalysis, which could change the path that the catalysts react with sulfur. Of course, to completely simulate the physical truth is almost impossible, however, it is still vital to reveal the active intermediates and the rate-determination step which mainly controlled the desulfurization rate in the catalytic reaction.

### 5.3. Hydrogen peroxide as the oxidant

Many researchers have investigated the mechanism of ODS with  $\text{H}_2\text{O}_2$  as the oxidizing agent. Concerning the reaction pathway over molecular sieve catalysts, most researchers suggested that  $\text{H}_2\text{O}_2$  was capable of interacting with catalyst surface sites to produce large numbers of superoxide radicals,<sup>87,145</sup> then these radicals reacted with DBT through a two-step oxidation mechanism producing DBTO and  $\text{DBTO}_2$ . Besides, the catalysts alone on the surface of mesoporous silica acted as the catalytic active sites (without  $\text{H}_2\text{O}_2$ ) could also oxidize DBT into sulfoxide or sulfone. E. Lorençon *et al.*<sup>145</sup> proposed an ODS mechanism over titanate nanotubes (TiNTs), in which surface-active Ti(IV) species reacted with  $\text{H}_2\text{O}_2$ , and produced corresponding sulfone ( $\text{DBTO}_2$ ) in acetonitrile phase (see Fig. 7).

Moreover, J. L. García-Gutiérrez<sup>146</sup> supposed that hydroperoxymolybdate group would be formed when  $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$  catalyst contacted with  $\text{H}_2\text{O}_2$ . They proposed a “nucleophilic attack” mechanism, according to the theory, hydroperoxymolybdate species were dehydrated to monoperoxo specie and diperoxo specie first; then the sulfur atom interacted with a peroxy group of mono- or diperoxo specie, in which sulfoxide and a regenerated monoperoxo or polymolybdate specie would be soon formed on the alumina surface. Finally, the sulfoxide reacted with a peroxide oxygen of molybdenum peroxy specie to produce sulfone. Meanwhile, another possible explanation of sulfur elimination using catalysts containing phosphate could be the following: the present of these electro-negative phosphate species adsorbed on the surface of alumina would confer the Mo(vi) atom with a higher electrophilic character and could effectively activate the  $\text{H}_2\text{O}_2$ .

Other researchers studied the mechanism of molecular sieve catalysts modified with ionic liquid. For the introduction of ionic liquid (IL), it is supposed that the catalyst would exhibit a somewhat hydrophobic property, which made the catalyst could exhibit excellent wettability for the model oil and could supply more exposure active sites to the reactants.<sup>147</sup> J. Zhuang *et al.*<sup>95</sup> established that imidazolium-based IL which has an uncoordinated N

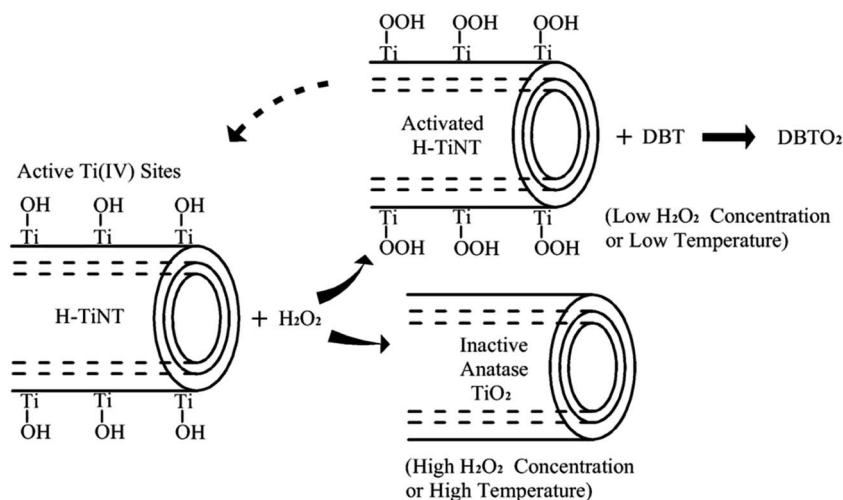


Fig. 7 Proposed mechanism for the oxidation of DBT by hydrogen titanate nanotubes.<sup>145</sup>

atom could keep higher Lewis acid sites in ODS reaction through strong electrostatic interactions. S. O. Ribeiro *et al.*<sup>148</sup> supported and further developed new views that the catalyst modified with ionic liquid had high oxidation ability though, which might cause undesired trouble when recycling the catalyst from the system, particularly in the case of liquid catalyst system. B. Jiang *et al.*<sup>149</sup> suggested that the H<sub>2</sub>O<sub>2</sub> oxidation rate was primarily determined by the concentration of peroxy-carboxylic acid in ionic liquids. A reaction mechanism which described fast oxidation of heterocyclic S-compounds with ionic liquid [HCPL][TFA] was developed and accepted (see Fig. 8). It suggested that [HCPL][TFA] had a slight advantages in acid strength among the amide-based TFA ionic liquids. The peroxy-carboxylic acid intermediate would be formed efficiently with [HCPL][TFA] during the ODS reaction. Formation of this peroxy-carboxylic acid species seemed to be a necessary step in ODS reaction, since the desulfurization performance depended on the forming rate of peroxy-carboxylic acid. D. Zheng *et al.*<sup>114</sup> presented a systematic research about involved chemical steps in DBT oxidation reaction over low-temperature-mediated titanium dioxide catalyst in ionic liquids.

The schematic summary of the photocatalytic performances of Ag/ALa<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> (A = Ca, Sr and Ba) with hydrogen peroxide is displayed in Fig. 9.<sup>150</sup> Results were demonstrated a novel desulfurization route. Firstly, the perovskite composite oxides would absorb photons through UV irradiation, which was different from the above-proposed oxidation processes that were conducted with ionic liquid-based catalysts or other molecular sieve catalysts. It further showed that the oxidation reaction between DBT and photocatalysts was dominated by the formation rate of excited electrons. Remarkably, the OH· was formed through the OH<sup>-</sup> interacting with holes or the O<sub>2</sub> reacting with excited electrons on the catalyst surface, then the DBT would be oxidized to sulfone with these OH· radicals which were reduced into CO<sub>2</sub> and H<sub>2</sub>O simultaneously. Accordingly, some researchers have proposed a general summary of the ODS chemistry over photocatalysts that emphasizes the key role of electrons.

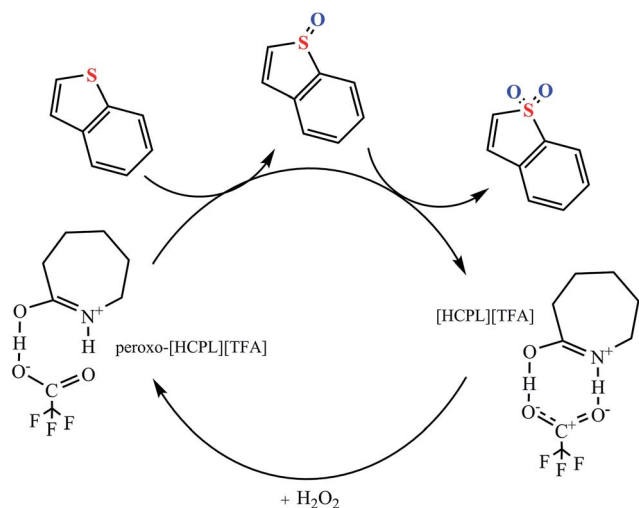


Fig. 8 Mechanism of fast oxidation of heterocyclic S-compounds with [HCPL][TFA].<sup>149</sup>

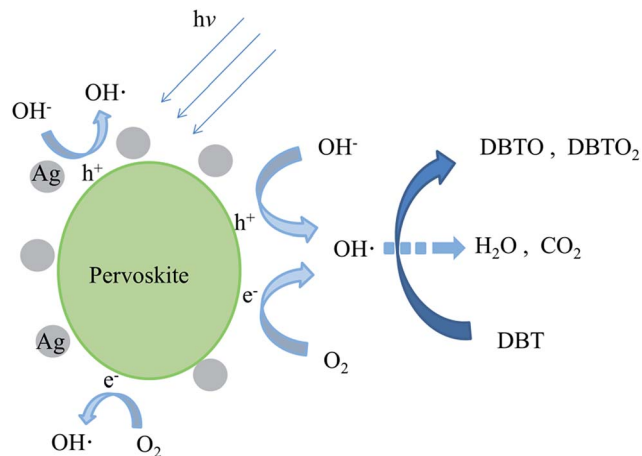
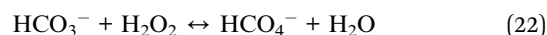


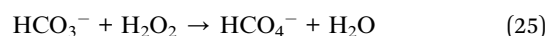
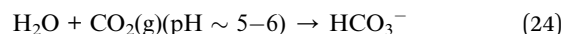
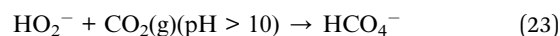
Fig. 9 Mechanism pathway of AlLa<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> (A = Ca and Ba) photocatalytic desulfurization.<sup>150</sup>

The bicarbonate-induced activation of H<sub>2</sub>O<sub>2</sub> could provide a metal-free choice for oxidative desulfurization,<sup>151</sup> and the basic DBT oxidation reaction steps over bicarbonate catalysts are as follows.

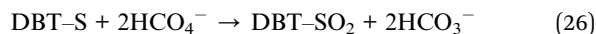
In the presence of NaCO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>,



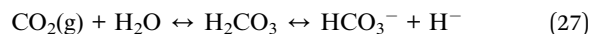
In the presence of CO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>,



HCO<sub>4</sub><sup>-</sup> oxidant is generated from the reaction between H<sub>2</sub>O<sub>2</sub> and NaHCO<sub>3</sub> (eqn (22)) or produced utilizing CO<sub>2</sub> gas as the bicarbonate precursor (eqn (23)), subsequently, HCO<sub>4</sub><sup>-</sup>-mediated oxidation is initiated to oxidize DBT to its corresponding oxide (eqn (26)).



Due to the aqueous acid-base equilibrium of CO<sub>2</sub>/HCO<sub>3</sub><sup>-</sup> (eqn (27)) needs efficient deprotonation of carbonic acid (H<sub>2</sub>CO<sub>3</sub>) to produce HCO<sub>3</sub><sup>-</sup> (and subsequently HCO<sub>4</sub><sup>-</sup>), DBT cannot be removed in the absence of NaOH.



This is considered as a practically affordable and eco-friendly method to achieve efficient desulfurization of real and model oil at room temperatures.

## 6. Conclusions and perspectives

This critical review on studies of catalytic oxidative desulfurization from oils as well as the kinetics and mechanisms has revealed the following trends.

(1) The supported catalysts are extremely crucial in the removal of sulfur from fuel oils for petroleum refinery and chemical plant at ambient conditions. Amounts of supported catalysts have been studied in the past decades. The heterogeneous catalysts using carriers have a better effect than homogeneous catalysts, with  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , mesoporous silicates, zeolite, SBA *etc.* as the carriers at ambient conditions.

(2) Catalysts deactivation is a problem that can not be ignored during the process of oxidation. Reaction parameters including the amounts of active components, the existence of N-containing compounds and the choice of reaction temperature would have tremendous impacts on catalysts activity. Besides, the effects of ODS on achieving ultra-clean oils are also deserve to be mentioned.

(3) The catalyst applied in ODS requires further improvement in its high stability, good selectivity as well as resistance of active component loss, N-containing compounds and high temperature. Maybe it can be obtained with catalysts by compounding the metal oxide and doping heteroatoms into appropriate carriers, such as  $\text{SiO}_2$ , mesoporous silicates and so on. At the same time, thanks to the improvement of analytical means and analog computation, the positive effects of supported catalysts and negative effects of inhibitors are hot topics in recent years.

(4) Some researches have been done to study the kinetics and mechanisms of the reaction and deactivation. The reactions of catalytic oxidation of sulfur compounds present in oils are of the first or quasi-first order of sulfur compounds. But the chemical reaction is, in most cases, of the first order on sulfur compounds. The first or quasi-first order of chemical reaction is in line with the Langmuir–Hinshelwood mechanism of homogeneous and heterogeneous catalytic reactions.

(5) The oxidation reaction of sulfur compounds is strongly temperature dependent, and the reaction rate constant ( $k$ ) is affected by many factors, such as substrate, catalyst and temperature *etc.* The catalytic activity order of the sulfur compounds are consistent with the apparent rate constant order. More importantly, the related reaction mechanism and kinetics could help us shed light on specific desulfurization process, vital rate-controlling step and inevitable catalyst deactivation.

Desulfurization of fuel oils by oxidation clearly carries lots of potential as the emerging carbon-neutral and green method that could be applied under ambient conditions. The fundamental chemistry of catalytic oxidation of several typical sulfur compounds present in fuel oils is necessary to be investigated, because desulfurization of the high sulfur fuel oils containing hundreds ppmw total sulfur could produce the ultra low sulfur fuel oils with tens ppmw total sulfur.

For the past few years, there was a surge of research into sustainable and environmentally benign catalytic oxidative desulfurization of fuel oils towards zero-sulfur fuels for industrial applications. The high selectivity of heterogeneous catalytic oxidation in certain reactions would allow production of the zero sulfur fuel oils from the feedstock with a relatively low concentration of sulfur compounds. There is a increasing trend of development of the advanced heterogeneous desulfurization

catalysts. The better characterization of those advanced materials could allow systematic improvements of their catalytic properties. Meanwhile, their mild selective oxidation towards the practicable chemicals is being explored.

Therefore, one of the goals of green organic chemistry,<sup>137–139</sup> *e.g.*, valorization of rather expensive oil feedstock to the higher-value chemicals *via* catalytic oxidative desulfurization, can be achieved. Although de-sulfur by catalytic oxidation has made tremendous achievements, the high selectivity efficiency, especially practical industrial application efficiency, remains to be further explored. Besides, the mechanism is also not totally clear and cannot effectively control the loss of active components and the poisoning of the desulfurization catalysts. The catalyst is limited for further wide applications and cannot lower the huge capital cost.

According to the specific exploration of the catalyst surface chemical reaction step, the mechanism of the de-sulfur can be fully proved, and its root cause of the deactivation and poisoning of the desulfurization catalyst can be found. Thus, fundamental studies on novel heterogeneous catalyst with excellent active sites distribution and its surface chemical process are needed. The modeling and design of the pilot scale desulfurization reactors is progressing, and much could be learned from the current researches of reaction engineering and the up-scaling of technologies of green catalysis in general.

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## References

- 1 A. Samokhvalov, *Catal. Rev.*, 2012, **54**, 281–343.
- 2 Y. Mathieu, L. Tzanis, M. Soulard, J. Patarin, M. Vierling and M. Molière, *Fuel Process. Technol.*, 2013, **114**, 81–100.
- 3 R. Trane, S. Dahl, M. S. Skjøth-Rasmussen and A. D. Jensen, *Int. J. Hydrogen Energy*, 2012, **37**, 6447–6472.
- 4 S. Dhir, R. Uppaluri and M. K. Purkait, *J. Hazard. Mater.*, 2009, **161**, 1360–1368.
- 5 I. S. Nashawi, A. Malallah and M. Al-Bisharah, *Energy Fuels*, 2010, **24**, 1788–1800.
- 6 S. Sorrell, J. Speirs, R. Bentley, A. Brandt and R. Miller, *Energy Policy*, 2010, **38**, 5290–5295.
- 7 L. Meng, C. P. Yang, H. M. Gan, T. Wu, G. M. Zeng and H. Chen, *Sep. Purif. Technol.*, 2008, **63**, 86–91.
- 8 H. Zhang, G. H. Huang and G. M. Zeng, *Environ. Pollut.*, 2009, **157**, 2413–2420.
- 9 Z. W. Li, G. M. Zeng, H. Zhang, B. Yang and S. Jiao, *Ecol. Modell.*, 2007, **202**, 540–546.
- 10 J. S. Pandey, R. Kumar and S. Devotta, *Atmos. Environ.*, 2005, **39**, 6868–6874.

- 11 M. Soleimani, A. Bassi and A. Margaritis, *Biotechnol. Adv.*, 2007, **25**, 570–596.
- 12 K. Haidong, W. Chit-Ming, V. V. Nuntavarn and Q. Zhengmin, *Environ. Res.*, 2010, **110**, 258–264.
- 13 V. T. Christoph, S. P. Michael, K. Stefan, K. Ernst, B. Meinolf and G. Klaus, *Toxicol. Lett.*, 2010, **196**, 42–50.
- 14 S. Weerasinghe, *Environmetrics*, 2010, **21**, 162–172.
- 15 H. N. Abubackar, F. R. Bengelsdorf, P. Dürre, M. C. Veiga and C. Kennes, *Appl. Energy*, 2016, **169**, 210–217.
- 16 N. A. B. Mabahwi, O. L. H. Leh and D. Omar, *Procedia - Social and Behavioral Sciences*, 2014, **153**, 221–229.
- 17 E. Ito and J. A. R. V. Veen, *Catal. Today*, 2006, **116**, 446–460.
- 18 E. S. Huh, A. Zazybin, J. Palgunadi, S. Ahn, J. Hong, H. S. Kim, M. Cheong and B. S. Ahn, *Energy Fuels*, 2009, **23**, 3032–3038.
- 19 A. Samokhvalov and B. J. Tatarchuk, *Catal. Rev.: Sci. Eng.*, 2010, **52**, 381–410.
- 20 T. A. Wierzbicki, I. C. Lee and A. K. Gupta, *Appl. Energy*, 2016, **165**, 904–918.
- 21 S. Kumar, H. T. Kwon, K. H. Choi, W. Lim, J. H. Cho, K. Tak and I. I. Moon, *Appl. Energy*, 2011, **88**, 4264–4273.
- 22 N. Abdoulmoumine, S. Adhikari, A. Kulkarni and S. Chattanathan, *Appl. Energy*, 2015, **155**, 294–307.
- 23 Z. R. Sun, B. H. Li, X. Hu, M. Shi, Q. N. Hou and Y. Z. Peng, *J. Environ. Sci.*, 2008, **20**, 268–272.
- 24 H. Shang, H. H. Zhang, W. Du and Z. H. Liu, *J. Ind. Eng. Chem.*, 2013, **19**, 1426–1432.
- 25 Z. Y. Jiang, H. Y. LÜ, Y. N. Zhang and C. Li, *Chin. J. Catal.*, 2011, **32**, 707–715.
- 26 Y. Shiraishi, K. Tachibana, T. Hirai and I. Komasa, *Ind. Eng. Chem. Res.*, 2002, **41**, 4362–4375.
- 27 S. E. Bonde, W. Gore, G. E. Dolbear and E. R. Skov, *Prepr. - Am. Chem. Soc., Div. Pet. Chem.*, 2000, **45**, 364–366.
- 28 D. Pant, D. Joshi, M. K. Upreti and R. K. Kotnala, *Waste Manag.*, 2012, **32**, 979–990.
- 29 R. T. Yang, A. J. Hernandez-Maldonado and F. H. Yang, *Science*, 2003, **301**, 79–81.
- 30 Z. X. Jiang, Y. Liu, X. P. Sun, F. P. Tian, F. X. Sun, C. H. Liang, W. S. You, C. R. Han and C. Li, *Langmuir*, 2003, **19**, 731–736.
- 31 X. L. Ma, L. Sun and C. S. Song, *Catal. Today*, 2002, **77**, 107–116.
- 32 M. J. K. Ahmed and M. Ahmaruzzaman, *Int. J. Environ. Sci. Technol.*, 2015, **12**, 1–10.
- 33 D. Pant and P. Singh, *J. Environ. Chem. Eng.*, 2013, **1**, 226–232.
- 34 D. Huang, Y. J. Wang, L. M. Yang and G. S. Luo, *Ind. Eng. Chem. Res.*, 2006, **45**, 1880–1885.
- 35 A. Tsyganok, C. M. Holt, S. Murphy, D. Mitlin and M. R. Gray, *Fuel*, 2011, **93**, 415–422.
- 36 N. S. Manan, L. Aldous, Y. Alias, P. Murray, L. J. Yellowlees, M. C. Lagunas and C. Hardacre, *J. Phys. Chem. B*, 2011, **115**, 13873–13879.
- 37 H. Y. Lü, J. B. Gao, Z. X. Jiang, Y. X. Yang, B. Song and C. Li, *Chem. Commun.*, 2007, **2**, 150–152.
- 38 S. Matsuzawa, J. Tanaka, S. Sato and T. Ibusuki, *J. Photochem. Photobiol., A*, 2002, **149**, 183–189.
- 39 K. Yazu, Y. Yamamoto, T. Furuya, K. Miki and K. Ukegawa, *Energy Fuels*, 2001, **15**, 1535–1536.
- 40 Z. R. Sun, H. Zhang, X. F. Wei, R. Du and X. Hu, *J. Electrochem. Soc.*, 2015, **162**, 9.
- 41 N. V. Borzenkova, I. A. Veselova and T. N. Shekhovtsova, *Biology Bulletin Reviews*, 2013, **3**, 296–311.
- 42 D. C. Bressler, B. K. Leskiw and P. M. Fedorak, *Can. J. Microbiol.*, 1999, **45**, 360–368.
- 43 H. Ichinose, M. Nakamizo, H. Wariishi and H. Tanaka, *Appl. Microbiol. Biotechnol.*, 2002, **58**, 517–526.
- 44 A. Caro, K. Boltes, P. Letón and E. García-Calvo, *Biochem. Eng. J.*, 2007, **35**, 191–197.
- 45 P. S. Tam, J. R. Kittrell and J. W. Eldridge, *Ind. Eng. Chem. Res.*, 1990, **29**, 324–329.
- 46 M. Te, C. Fairbridge and Z. Ring, *Appl. Catal., A*, 2001, **219**, 267–280.
- 47 L. F. Ramírez-Verduzco, E. Torres-García, R. Gómez-Quintana, V. González-Peña and F. Murrieta-Guevara, *Catal. Today*, 2004, **98**, 289–294.
- 48 F. M. Collins, A. R. Lucy and C. Sharp, *J. Mol. Catal. A: Chem.*, 1997, **117**, 397–403.
- 49 S. Otsuki, T. Nonaka, N. Takashima, W. Qian, A. Ishihara, T. Imai and T. Kabe, *Energy Fuels*, 2000, **14**, 1232–1239.
- 50 W. Gore, S. Bonde, G. E. Dolbear and E. R. Skov, *US Pat.*, 6596914, 2003.
- 51 S. Murata, K. Murata, K. Kidena and M. Nomura, *Energy Fuels*, 2004, **18**, 116–121.
- 52 G. P. Khare and E. L. Sughrue, *US Pat.*, 20040004029, 2004.
- 53 H. Mei, B. W. Mei and T. F. Yen, *Fuel*, 2003, **82**, 405–414.
- 54 A. M. Dehkordi, M. A. Sobati and M. A. Nazem, *Chin. J. Chem. Eng.*, 2009, **17**, 869–874.
- 55 V. R. Tumula, S. Bondwal, P. Bisht, C. Pendem and J. Kumar, *React. Kinet., Mech. Catal.*, 2012, **107**, 449–466.
- 56 A. D. Giuseppe, M. Crucianelli, F. D. Angelis, C. Crestini and R. Saladino, *Appl. Catal., B*, 2009, **89**, 239–245.
- 57 V. Hulea, A. L. Maciucă, A. M. Cojocariu, C. E. Ciocan and E. Dumitriu, *C. R. Chim.*, 2009, **12**, 723–730.
- 58 Z. Hasan, J. Jeon and S. H. Jhung, *J. Hazard. Mater.*, 2012, **205–206**, 216–221.
- 59 X. C. Li, S. X. Huang, Q. R. Xu and Y. F. Yang, *Transition Met. Chem.*, 2009, **34**, 943–947.
- 60 D. Kim, K. Y. Kim, H. D. Ryu, K. K. Min and S. I. Lee, *Bioresour. Technol.*, 2009, **100**, 3180–3184.
- 61 D. Kim, J. Kim, H. D. Ryu and S. I. Lee, *Bioresour. Technol.*, 2009, **100**, 74–78.
- 62 J. Z. Zhang, J. B. Li, R. W. Thring, X. Hu and X. Y. Song, *J. Hazard. Mater.*, 2012, **203–204**, 195–203.
- 63 A. Ishihara, D. H. Wang, F. Dumeignil, H. Amano, E. W. Qian and T. Kabe, *Appl. Catal., A*, 2005, **279**, 279–287.
- 64 A. Chica, A. Corma and M. E. Dómine, *J. Catal.*, 2006, **242**, 299–308.
- 65 J. Chang, A. Wang, J. Liu, X. Li and Y. K. Hu, *Catal. Today*, 2010, **149**, 122–126.
- 66 J. T. Sampanthar, X. Huang, D. Jian, T. Y. Nah, R. Xu and W. P. Kwan, *Appl. Catal., B*, 2006, **63**, 85–93.
- 67 G. X. Yu, S. X. Lu, H. Chen and Z. N. Zhu, *Energy Fuels*, 2005, **19**, 447–452.

- 68 Z. X. Jiang, H. Y. LÜ, Y. N. Zhang and C. Li, *Chin. J. Catal.*, 2011, **32**, 707–715.
- 69 F. Zannikos, E. Lois and S. Stournas, *Fuel Process. Technol.*, 1995, **42**, 35–45.
- 70 K. Yazu, M. Makino and K. Ukegawa, *Chem. Lett.*, 2004, **33**, 1306–1307.
- 71 D. Huang, Y. J. Wang, L. M. Yang and G. S. Luo, *Ind. Eng. Chem. Res.*, 2006, **45**, 1880–1885.
- 72 D. H. Wang, E. W. Qian, H. Amano, K. Okata, A. Ishihara and T. Kabe, *Appl. Catal., A*, 2003, **253**, 91–99.
- 73 N. W. A. Wan, R. Ali and A. W. A. B. Wan, *J. Taiwan Inst. Chem. Eng.*, 2016, **58**, 344–350.
- 74 L. Cedeno-Caero, H. Gomez-Bernal, A. Fraustro-Cuevas, H. D. Guerra-Gomez and R. Cuevas-Garcia, *Catal. Today*, 2008, **133–135**, 244–254.
- 75 S. Varghese, M. G. Cutrufello, E. Rombi, R. Monaci, C. Cannas and I. Ferino, *J. Porous Mater.*, 2014, **21**, 539–549.
- 76 R. Gómez-Reynoso, J. Ramírez, R. Nares, R. Luna and F. Murrieta, *Catal. Today*, 2005, **107–108**, 926–932.
- 77 V. V. D. N. Prasad, K. E. Jeong, H. J. Chae, C. U. Kim and S. Y. Jeong, *Catal. Commun.*, 2008, **9**, 1966–1969.
- 78 A. Bazyari, A. A. Khodadadi, A. H. Mamaghani, J. Beheshtian, L. T. Thompson and Y. Mortazavi, *Appl. Catal., B*, 2016, **180**, 65–77.
- 79 X. H. Han, A. J. Wang, X. S. Wang, X. Li, Y. Wang and Y. K. Hu, *Catal. Commun.*, 2013, **42**, 6–9.
- 80 J. M. Fraile, C. Gil, J. A. Mayoral, B. Muel, L. Roldán, E. Vispe, S. Calderón and F. Puente, *Appl. Catal., B*, 2016, **180**, 680–686.
- 81 Z. Jian, A. Wang, Y. Wang, H. Wang and J. Gui, *Chem. Eng. J.*, 2014, **245**, 65–70.
- 82 S. H. Xun, W. S. Zhu, D. Zheng, L. Zhang, H. Liu, S. Yin, M. Zhang and H. M. Li, *Fuel*, 2014, **136**, 358–365.
- 83 M. Li, M. Zhang, A. Wei, W. S. Zhu, S. H. Xun, Y. N. Li, H. P. Li and H. M. Li, *J. Mol. Catal. A: Chem.*, 2015, **406**, 23–30.
- 84 B. S. Li, K. Wu, T. H. Yuan, C. Y. Han, J. Q. Xu and X. M. Pang, *Microporous Mesoporous Mater.*, 2012, **151**, 277–281.
- 85 V. Hulea, P. Moreau and F. D. Renzo, *J. Mol. Catal. A: Chem.*, 1996, **111**, 325–332.
- 86 D. Nedumaran and A. Pandurangan, *Mater. Res. Bull.*, 2015, **61**, 1–8.
- 87 D. Xie, Q. H. He, Y. Y. Su, T. W. Wang, R. F. Xu and B. X. Hu, *Chin. J. Catal.*, 2015, **36**, 1205–1213.
- 88 H. Kim, H. S. Kim, K. E. Jeong, S. Y. Jeong, Y. K. Park and J. K. Jeon, *Res. Chem. Intermed.*, 2010, **36**, 669–676.
- 89 R. Huirache-Acuña, B. Pawelec, E. Rivera-Muñoz, R. Nava, J. Espino and J. L. G. Fierro, *Appl. Catal., B*, 2009, **92**, 168–184.
- 90 R. Nava, R. A. Ortega, G. Alonso, C. Ornelas, B. Pawelec and J. L. G. Fierro, *Catal. Today*, 2007, **127**, 70–84.
- 91 C. X. Shi, W. X. Wang, N. Liu, X. Y. Xu, D. H. Wang, M. H. Zhang, P. C. Sun and T. H. Chen, *Chem. Commun.*, 2015, **51**, 11500–11503.
- 92 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*, 2012, **4**, 687–697.
- 93 J. Yang, X. H. Yu, J. Y. Yan, S. T. Tu and E. Dahlquist, *Appl. Energy*, 2013, **112**, 755–764.
- 94 Y. K. Hu, J. Y. Yan and H. L. Li, *Appl. Energy*, 2012, **97**, 255–263.
- 95 J. Z. Zhuang, X. Y. Jin, X. L. Shen, J. J. Tan, L. H. Nie, J. Xiong and B. Hu, *Bull. Korean Chem. Soc.*, 2015, **36**, 1784–1790.
- 96 M. Chamack, A. R. Mahjoub and H. Aghayan, *Chem. Eng. J.*, 2014, **255**, 686–694.
- 97 A. T. Shah, B. S. Li and Z. E. A. Abdalla, *J. Colloid Interface Sci.*, 2009, **336**, 707–711.
- 98 O. González-García and L. Cedeño-Caero, *Catal. Today*, 2009, **148**, 42–48.
- 99 S. Li and J. S. Lee, *J. Catal.*, 1998, **178**, 119–136.
- 100 G. J. Wang, Y. F. Han, F. Wang, Y. P. Chu and X. T. Chen, *React. Kinet., Mech. Catal.*, 2015, **115**, 679–690.
- 101 L. C. Caero, J. F. Navarro and A. Gutiérrez-Alejandre, *Catal. Today*, 2006, **116**, 562–568.
- 102 Y. H. Jia, G. Li, G. L. Ning and C. Z. Jin, *Catal. Today*, 2009, **140**, 192–196.
- 103 H. S. Cheong, K. K. Kang and H. K. Rhee, *Catal. Lett.*, 2003, **86**, 145–149.
- 104 S. Y. Jiang, Y. Kong, J. Wang, X. Q. Ren and Q. J. Yan, *J. Porous Mater.*, 2006, **13**, 341–346.
- 105 T. Tatsumi, Y. Watanabe, Y. Hirasawa and J. Tsuchiya, *Res. Chem. Intermed.*, 1998, **24**, 529–540.
- 106 J. H. Kim, X. L. Ma, A. N. Zhou and C. S. Song, *Catal. Today*, 2006, **111**, 74–83.
- 107 K. S. Cho and Y. K. Lee, *Appl. Catal., B*, 2014, **147**, 35–42.
- 108 E. Rafiee and N. Rahpeyma, *Chin. J. Catal.*, 2015, **36**, 1342–1349.
- 109 X. C. Chen, S. Yuan, A. A. Abdeltawab, S. S. Al-Deyab, J. W. Zhang, L. Yu and G. R. Yu, *Sep. Purif. Technol.*, 2014, **133**, 187–193.
- 110 L. Yang, S. Q. Wang, R. C. Wang and H. B. Yu, *Chin. J. Chem. Eng.*, 2013, **21**, 558–563.
- 111 D. H. Wang, N. Liu, J. Y. Zhang, X. Zhao, W. H. Zhang and M. H. Zhang, *J. Mol. Catal. A: Chem.*, 2014, **393**, 47–55.
- 112 L. T. Li, J. S. Zhang, C. Shen, Y. J. Wang and G. S. Luo, *Fuel*, 2016, **167**, 9–16.
- 113 T. T. Wang, Y. Lu, H. L. Wu and E. B. Wang, *Inorg. Chim. Acta*, 2016, **446**, 13–18.
- 114 D. Zheng, W. S. Zhu, S. H. Xun, M. M. Zhou, M. Zhang, W. Jiang, Y. J. Qin and H. M. Li, *Fuel*, 2015, **159**, 446–453.
- 115 J. Xiao, L. M. Wu, Y. Wu, B. Liu, L. Dai, Z. Li, Q. B. Xia and H. X. Xi, *Appl. Energy*, 2014, **113**, 78–85.
- 116 U. Arellano, J. A. Wang, M. T. Timko, L. F. Chen, S. P. P. Carrera, M. Asomoza, O. A. González Vargas and M. E. Llanos, *Fuel*, 2014, **126**, 16–25.
- 117 Z. Y. Long, C. P. Yang, G. M. Zeng, L. Y. Peng, C. H. Dai and H. J. He, *Fuel*, 2014, **130**, 19–24.
- 118 K. Zhao, Y. Cheng, H. Y. Liu, C. P. Yang, L. Qiu, G. M. Zeng and H. J. He, *RSC Adv.*, 2015, **5**, 66013–66023.
- 119 L. Qiu, Y. Cheng, C. P. Yang, G. M. Zeng, Z. Y. Long, S. N. Wei and L. Luo, *RSC Adv.*, 2016, **6**, 17036–17045.
- 120 N. Zang, X. M. Qian, R. Huang and C. M. Shu, *Thermochim. Acta*, 2013, **568**, 175–184.



- 121 C. P. Yang, K. Zhao, Y. Cheng, G. M. Zeng, M. M. Zhang, J. J. Shao and L. Lu, *Sep. Purif. Technol.*, 2016, **163**, 153–161.
- 122 L. Y. Kong, G. Li and X. S. Wang, *Catal. Lett.*, 2004, **92**, 163–167.
- 123 F. T. Li, R. H. Liu, Z. M. Sun and D. S. Zhao, *Bioinformatics and Biomedical Engineering*, 2008, **2**, 3887–3890.
- 124 D. Zhao, J. Zhang, J. Wang, W. Liang and H. Li, *Pet. Sci. Technol.*, 2009, **27**, 1–11.
- 125 J. Zhang, D. S. Zhao, J. L. Wang and L. Y. Yang, *J. Mater. Sci.*, 2009, **44**, 3112–3117.
- 126 F. T. Li, Z. M. Sun, Y. Liu, D. Zhao and R. Liu, *China Pet. Process. Petrochem. Technol.*, 2009, **4**, 48–52.
- 127 J. Zhang, D. Zhao, L. Y. Yang and Y. B. Li, *Chem. Eng. J.*, 2010, **156**, 528–531.
- 128 D. S. Zhao, F. T. Li, E. P. Zhou and Z. M. Sun, *Chem. Res. Chin. Univ.*, 2008, **24**, 96–100.
- 129 F. T. Li, R. H. Liu, Z. M. Sun and D. S. Zhao, *Bioinformatics and Biomedical Engineering*, 2008, **2**, 3762–3765.
- 130 R. Vargas and O. Núñez, *J. Mol. Catal. A: Chem.*, 2008, **294**, 74–81.
- 131 W. S. Zhu, G. P. Zhu, H. M. Li, Y. H. Chao, M. Zang, D. L. Du, Q. Wang and Z. Zhao, *Fuel Process. Technol.*, 2013, **106**, 70–76.
- 132 J. Robertson and T. J. Bandoz, *J. Colloid Interface Sci.*, 2006, **299**, 125–135.
- 133 A. E. S. Choi, S. Roces, N. Dugos and M. W. Wan, *Fuel*, 2016, **180**, 127–136.
- 134 G. Q. Luo, L. H. Kang, M. Y. Zhu and B. Dai, *Fuel Process. Technol.*, 2014, **118**, 20–27.
- 135 J. H. Qiu, G. H. Wang, D. L. Zeng, Y. Tang, M. Wang and Y. J. Li, *Fuel Process. Technol.*, 2009, **90**, 1538–1542.
- 136 Y. Nie, Y. X. Dong, L. Bai, H. F. Dong and X. P. Zhang, *Fuel*, 2013, **103**, 997–1002.
- 137 B. Saha and S. Sengupta, *Fuel*, 2015, **150**, 679–686.
- 138 O. Levenspiel, *J. Catal.*, 1972, **25**, 265–272.
- 139 F. L. Yu, C. Y. Liu, B. Yuan, C. X. Xie and S. T. Yu, *Catal. Commun.*, 2015, **68**, 49–52.
- 140 S. C. Chen, W. Y. Lu, Y. Y. Yao, H. X. Chen and W. X. Chen, *React. Kinet., Mech. Catal.*, 2013, **111**, 535–547.
- 141 S. Murata, K. Murata, K. Kidena and M. Nomura, *Energy Fuels*, 2004, **18**, 116–121.
- 142 W. N. W. Abdullah, W. A. W. Abu Bakar and R. Ali, *Korean J. Chem. Eng.*, 2015, **32**, 1999–2006.
- 143 W. A. W. Abu Bakar, R. Ali, A. A. A. Kadir and W. N. A. W. Mokhtar, *Fuel Process. Technol.*, 2012, **101**, 78–84.
- 144 P. J. Kropp, G. W. Breton, J. D. Fields, J. C. Tung and B. R. Loomis, *J. Am. Chem. Soc.*, 2000, **122**, 4280–4285.
- 145 E. Lorençon, D. C. B. Alves, K. Krambrock, E. S. Ávila, R. R. Resende, A. S. Ferlauto and R. M. Lago, *Fuel*, 2014, **132**, 53–61.
- 146 J. L. García-Gutiérrez, G. A. Fuentes, M. E. Hernández-Terán, P. García, F. Murrieta-Guevara and F. Jiménez-Cruz, *Appl. Catal., A*, 2008, **334**, 366–373.
- 147 J. Xiong, W. S. Zhu, W. J. Ding, L. Yang, Y. H. Chao, H. P. Li, F. X. Zhu and H. M. Li, *Ind. Eng. Chem. Res.*, 2014, **53**, 19895–19904.
- 148 S. O. Ribeiro, D. Julião, L. Cunha-Silva, V. F. Domingues, R. Valença, J. C. Ribeiro, B. D. Castro and S. S. Balula, *Fuel*, 2016, **166**, 268–275.
- 149 B. Jiang, H. W. Yang, L. H. Zhang, R. Y. Zhang, Y. L. Sun and Y. Huang, *Chem. Eng. J.*, 2016, **283**, 89–96.
- 150 N. Zhao, S. W. Li, X. Zhang, X. Y. Huang, J. Y. Wang, R. M. Gao, J. S. Zhao and J. L. Long, *Colloids Surf., A*, 2015, **481**, 125–132.
- 151 A. D. Bokare and W. Choi, *J. Hazard. Mater.*, 2015, **304**, 313–319.