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Deoxydesulfurization of liquid fuels using air assisted performic acid oxidation followed by reductive decomposition through *in situ* generated Ni-boride†

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The deoxydesulfurization of organosulfur compounds in model and commercial oil was investigated by oxidation with performic acid followed by reduction with *in situ* generated Ni_2B under ambient conditions. The desulfurization efficiency of the process is high and is superior to the extractive ODS, since it does not require a large quantity of solvent for the extraction and also the parent hydrocarbons of the organosulfur compounds are returned to the feed, thereby avoiding loss of oil.

Because of the mild operating conditions, oxidative desulfurization (ODS) is attaining great popularity as an alternative technology to commercial hydrodesulfurization (HDS) to overcome environmental problems associated with sulfur compounds, which are prevalent in liquid fuels. In the ODS process the sulfur compounds in petroleum are oxidized using an appropriate oxidation route, and the oxidized products are removed by extraction or adsorption, owing to their increased polarity.[1] The oxidized sulfur compounds are treated as waste, but for a commercially acceptable process it is necessary to decompose these compounds and return the residual products to the oil, in order to avoid loss in yield.

A number of methods have been reported for the decomposition of sulfones to the respective hydrocarbons, such as the catalytic decomposition of sulfones at high temperature and pressure in the presence of MgO supported on mesoporous silica or alumina,[2] or Cs over MCM-41.[3] Nickel complexes in the presence of methyl magnesium bromide were reported to decompose a variety of benzothiophene sulfones in toluene and THF under reflux.[4] Similarly, different types of benzothiophene sulfones are decomposed under harsh conditions, using metallic Na and liquid NH_3,[5] NiCRA's,[6] Mg in methanol,[7] metallic Zn or $LiAlH_4$.[8,9] Lithium and sodium were also reported to cause the decomposition of DBT sulfones in dioxane under reflux for 24 h.[10] However, the methods reported earlier have some shortcomings, such as requiring harsh conditions (high temperature and pressure), long reaction times or excess of protic solvent systems *etc*. Besides, these methods are based on the isolation of sulfones and treating them separately.

We report here a two stage ODS process for the desulfurization of a model oil (sulfur content of 1275 $\mu g\ g^{-1}$), containing thiophene (2000 $\mu g\ g^{-1}$), dibenzothiophene (2000 $\mu g\ g^{-1}$) and 4-methyl dibenzothiophene (1000 $\mu g\ g^{-1}$) dissolved in *n*-heptane, as well as of commercial oil samples. The commercial oil samples used in this study include untreated naphtha, light gas oil (LGO) and cooker combined heavy gas oil (HGO), with a total sulfur content of 2, 1.2, and 4 wt%, respectively.

In the first step, the sulfur compounds are oxidized using hydrogen peroxide and formic acid assisted by air oxidation, whereas the second step involves the decomposition of sulfones by Ni-boride generated *in situ* in the same reaction medium, containing the oxidation mixture. The desulfurization efficiency of ODS followed by solvent extraction and ODS followed by catalytic decomposition is also compared.

In a typical oxidation experiment, a (20 ml) model oil was oxidized by 30% hydrogen peroxide (1.5 ml) and formic acid (2 ml) in a three neck flask, at a temperature of 60 °C and 60 min reaction time, with continuous magnetic stirring. Compressed dried air was bubbled with a flow rate of 150 ml min^{-1} through a pyrex glass bubbler. After oxidation, one batch of the oxidized model oil was shifted to a separating funnel and was extracted with an equal quantity of methanol–water mixture (80 : 20). To the next batch of the oxidized model oil, Ni chloride (3.5 mmol) dissolved in 5 ml of methanol was added and stirred for 5 min, followed by addition of $NaBH_4$ (0.015 mmol) and stirred for additional 30 min at room temperature. A black fine precipitate was formed, with evolution of hydrogen gas. The catalytic decomposition of the sulfur compounds in the model oil was also carried out without prior oxidation. The total sulfur content was analyzed by a S and N analyzer (Antek by PAL), equipped with a chemiluminscent and vacuum UV detector. The furnace temperature was 3000 °C. Argon was used as the carrier gas and pure oxygen gas as the oxidant. The concentrations of thiophene, DBT and 4-MDBT in the model oil were determined by an Agilent 7890A gas chromatograph (GC), equipped with a flame ionization

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detector (FID), PIONA capillary column (25 m × 0.25 μm) and autosampler.

The effect of the reaction temperature on the oxidative conversion of model sulfur compounds is shown in Table 1, which indicates that the conversion rate increases with an increase in temperature. It is also evident from the data that the trend in oxidation reactivity of the model compounds is as follows: thiophene < DBT < 4-MDBT. During the oxidation process, performic acid is formed by the reaction of H_2O_2 and HCOOH. The performic acid oxidizes the sulfur compounds into sulfoxides, and then sulfones. The products formed in the current process were only the sulfones respective to the model sulfur compounds, which have been confirmed by GC-MS analysis in the laboratory. As air cannot directly oxidize sulfur compounds, it can participate in the oxidation only when it forms a hydroperoxide from the hydrocarbon molecule present in the medium. In the case of the model oil, *n*-heptane is resistant to autoxidation under the current temperature, which is lower than 100 °C, however, it acts as a co-oxidant with performic acid.

The results shown in Table 2 indicate that the desulfurization yield of the extractive ODS process was 87.92%, whereas the yield of the process involving the oxidation of model oil followed by catalytic decomposition with Ni_2B was 88.67%. It is evident from these results that the efficiency of both the processes was almost the same. However, in the former process the spent solution contains sulfones, whereas in the latter process the sulfones are decomposed into the parent hydrocarbons with elimination of the sulfur atom. The reaction involves the formation of solid Ni_2B and gaseous H_2, from the reaction of $NiCl_2$ and $NaBH_4$ in the presence of methanol. The highly reactive hydrogen is adsorbed onto the surface of Ni_2B, which attacks the αC and results in the C–S bond cleavage (Scheme 1).[11]

Furthermore, it was found that the desulfurization yield of the model oil was very low for the direct reduction with Ni_2B without prior oxidation, as compared to the oxidation followed by reduction route. Upon the direct reduction of the model oil, the rate of decomposition of the sulfur compounds was very poor, but in the oxidation followed by reduction route, it increased significantly (Scheme 1).

Using the direct reduction route, the % reductive decomposition of thiophene, DBT and 4-MDBT was found to be 57, 53 and 68%, respectively (Fig. 1). However, in the process involving prior oxidation followed by reduction, the decomposition of thiophene, DBT and 4-MDBT was 86, 88, and 96%, respectively. These results show that the ease of the C–S bond cleavage increases when S is oxidized to the respective sulfones and sulfoxides. In other words, due to the S–O linkage in the oxidized sulfur compounds, the neighbouring C–S bond weakens, and can be easily cleaved by reduction as compared to a normal C–S bond. This phenomenon was explained by Gilman,[12] who proposed that during the course of the decomposition of DBT sulfones, the dianion intermediate formed is stabilized, which is not the case for DBT. Therefore, the yield of biphenyl by decomposition of DBT sulfone is more than that of DBT.

Table 1 Oxidative conversion of model sulfur compounds using anair assisted performic acid oxidation system

	% Conversion at different temperatures		
Sulfur compounds	40 °C	60 °C	80 °C
Thiophene	47	78	94
DBT	73	96	98
4-MDBT	87	98	99

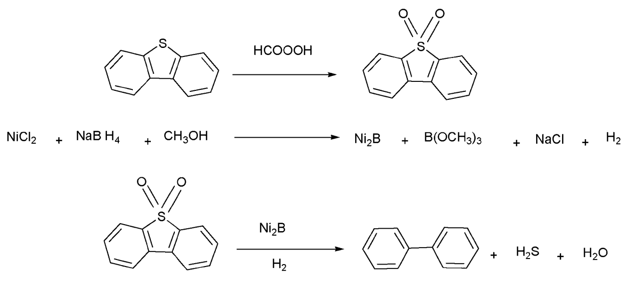
Table 2 Desulfurization efficiency of ODS followed by extraction and by catalytic decomposition

Treated sample	Sulfur content (μg g^{-1})[a]	% Desulfurization
ODS followed by extraction with MeOH	154.1 ± 1.4	87.9
ODS followed by reduction with Ni-boride	144.5 ± 0.62	88.7

[a] Sulfur content in model oil 1275 (μg g^{-1}).

The reduction with Ni_2B requires a protic medium, which is provided in excess when carried out in an oxidation medium, *i.e.* in the presence of aqueous formic acid solution. Additionally, sulfones have high reactivity towards reduction, thus a high desulfurization yield is attained in the process. In the case of the reduction without oxidation, the same medium in not available and the quantity of methanol available is very small (merely used for the dissolution of $NiCl_2$), which is insufficient for the reduction, and leads to a low desulfurization efficiency. Therefore, the current process involving oxidation followed by reduction does not need additional protic solvents.

Next, we carried out desulfurization of commercial oil samples, *i.e.* untreated naphtha, light gas oil (LGO) and heavy gas oil (HGO), through oxidation followed by extraction, as well as oxidation followed by reduction. The oxidation of commercial oil (20 ml) was carried out in a 100 ml three neck flask, to which hydrogen peroxide (2 ml) and formic acid (2 ml) were added, and was magnetically stirred (750 rpm speed) with continuous air bubbling (150 ml min^{-1}) for 60 min at a temperature of 60 °C. In the case of HGO, 5 ml benzene was also added to reduce the viscosity of the feed and facilitate the mixing of the oxidant and oil. A batch of oxidized oil was extracted with an acetonitrile–water mixture (80 : 20) followed by another extraction with a methanol–water mixture (80 : 20). To another batch of oxidized oil, Ni chloride (3.5



Scheme 1 Reaction scheme of deoxydesulfurization using Ni_2B.

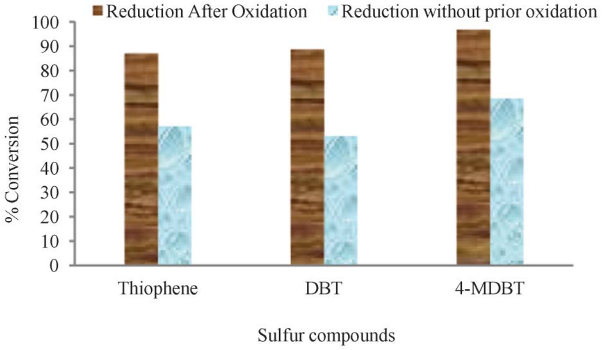


Fig. 1 Reactivity of different sulfur compounds towards reduction, after oxidation and without oxidation.

m mol) dissolved in 5 ml of methanol was added and stirred for 5 min, then solid $NaBH_4$ (0.015 m mol) was added and further stirred at room temperature for about 30 min. The oil phases collected in both processes were subjected to total S analysis. The results show that when using oxidation followed by extraction, the desulfurization yield of untreated naphtha, LGO and HGO was 59, 61 and 45%, respectively, whereas in the case of oxidation followed by reduction it was found to be 55, 60 and 42%, respectively. These results indicate that the desulfurization yield of both processes is comparable. However, in the case of the extractive ODS, the extraction process leads to a considerable loss of feed, and hence reduces the oil recovery. The problem is more severe in the case of heavy oils, for which the extraction is a tedious job, leading to oil loss and increase in the viscosity of the feed. Besides, for deep desulfurization of commercial fuels multiple extractions are required. In extractive ODS, the extracted sulfones are collected as waste, which needs additional processing and treatment.

In the current deoxydesulfurization process the sulfones are directly decomposed with the elimination of a sulfur atom in the form of H_2S, therefore, the loss of oil during the process is negligible. The aqueous phase can be easily separated from the oil phases by gravity separation or fractional distillation. However, more work is needed in this field to improve the process efficiency.

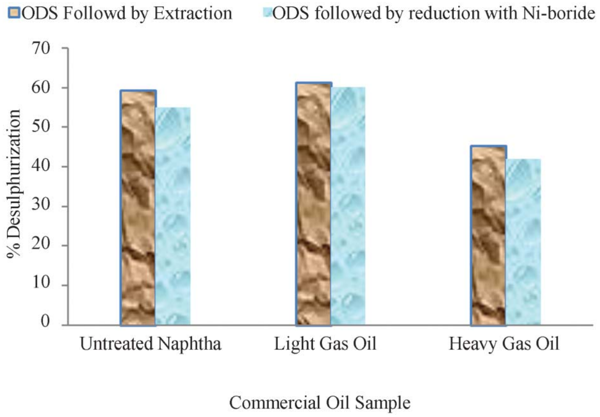


Fig. 2 Comparative efficiency of extractive ODS and reductive ODS.

Conclusions

Deoxydesulfurization of model oil and commercial oil by oxidation of sulfur compounds followed by reduction with Ni_2B catalyst, generated *in situ* from the reaction of $NaBH_4$ and $NiCl_2$, is an efficient process, and an alternative to extractive ODS. In comparison to the direct desulfurization by reduction, the conversion of model sulfur compounds was increases by 35 to 45% when model oil was first oxidized and then reduced. The reduction based ODS process shows high efficiency without requiring large quantities of solvent for extraction, and also loss of oil is avoided since the parent hydrocarbons of the organosulfur compounds are returned to the oil phase.

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