Deep Oxidative Desulfurization of Fuels Using Na$_2$WO$_4$.2H$_2$O in Acidic Ionic Liquids

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Abstract The catalytic oxidation desulfurization system of commercially available Na$_2$WO$_4$.2H$_2$O and phase transfer catalyst has been found suitable for deep removal of organic sulfur in fuels with H$_2$O$_2$ as oxidant in acidic ionic liquid. Under the optimal conditions, the sulfur removal could reach almost 100%. Moreover, this acidic ionic liquid can be recycled five times by distillation without obviously decrease in activity. Meanwhile, the problem of the mutual solubility between the acidic ionic liquid and model oil and the mechanism of oxidation desulfurization were also elaborated.

Keywords: acidic ionic liquid, catalytic oxidation, desulfurization, phase transfer catalyst

Introduction

In the past decades, sulfur compounds in transportation fuels have been a principal source of air pollution due to the growing number of cars. Therefore, many stringent environment legislations have been regulated to limit the sulfur content of fuels(**He, Li et al. 2008**); For example, many western countries have mandated a reduction in fuels sulfur level to 10 ppm by 2009(**Babich and Moulijn 2003**). Consequently, the deep desulfurization of fuels has attracted increased attention in the worldwide(**Huang, Chen et al. 2004**). The hydrodesulfurization (HDS) process has been widely used to remove various sulfur-containing compounds from gas oil or diesel fuels, such as thiols, sulfides, and disulfides to low sulfur content in oil. However, HDS is hard to remove refractory sulfur-containing compounds like dibenzothiophene (DBT) and its derivatives to meet the new stricter regulations(**Zhao, Liu et al. 2008**), to achieve deep desulfurization through typical HDS require severe condition include high temperature (>300℃), high hydrogen pressure (>4Mpa) and more-active catalysts, which lead to higher investment and operating cost(**Li, Jiang et al. 2009**), So it is necessary to develop new approaches to deep desulfurization of liquid hydrocarbon fuels. Thus, alternative sorts of desulfurization, such as oxidative desulfurization (ODS)(**Zhou, Li et al. 2009**), biodesulfurization(**Soleimani, Bassi et al. 2007**), extractive desulfurization with ionic liquids(**Nie, Li et al. 2007**), and selective adsorptive desulfurization(**Shan, Liu et al. 2008**), have attracted many researchers' interesting. Compared with these methods(**Liu, Wang et al. 2008**), oxidative desulfurization (ODS) has been considered to be one of the promising

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alternative methods for desulfurization, because it can be performed under mild conditions to remove the refractory sulfur compounds, such as dibenzothiophene (DBT) and its derivatives (DBTs). In recent papers and patents, various oxidation systems have been reported, the oxidizing agents for ODS are H_2O_2(**Lu, Cheng et al. 2007**), nitric acid/NO_2(**Guru 2007**), peracids(**Lo, Yang et al. 2003**), t-BuOOH and O_2 or O_3. Among those oxidants, hydrogen peroxide has been widely used, for it does not pollute the environment, the only byproduct is water(**Noyori, Aoki et al. 2003**) and high oxygen availability(**Weng, Wang et al. 2008**).Although these ODS processes can effectively remove sulfur compounds; one of the primary concerns is that a large amount of volatile and flammable organic compounds (VOCs) are employed as extractants(**Lo, Yang et al. 2003**).

Room temperature ionic liquids (RTILs) are considered as "green solvents" and environmentally benign alternative solvents for catalysis, organic synthesis, and separations due to their advantageous properties such as negligible vapor pressure, high thermal and chemical stability(**Gordon 2001**)etc. Along with the quick development of room temperature ionic liquids, various kinds of ionic liquids used as extractants and solvents have been reported. SO_3H-functionalized acidic ionic liquids were first taken as dual solvent-catalysts such as esterification(**Cole, Jensen et al. 2002**)and oxidation of cyclohexene(**Gui, Liu et al. 2005**), in which this type of ionic liquids showed high selectivity and catalytic activity. However, For Little research attention has been paid to the utilization of acidic ionic liquid reagent in desulfurization systems. Lu(**Lu, Cheng et al. 2007**) and Zhao(**Zhao, Wang et al. 2007**) first use acidic ionic liquid ([HMim]BF_4 and [Hnmp]BF_4) and H_2O_2 in the desulfurization field. The results of these experiments show that the acidic ionic liquid not only served as extractant and reaction media but also improved the catalytic activity of the desulfurization effectively. Ryoji Noyori(**Noyori, Aoki et al. 2003**)found that when coupled with a tungstate complex and quaternary ammonium hydrogensulfate as an acidic phase-transfer catalyst.Aldehydes are oxidized to carboxylic acids and corresponding carbonyl compounds efficiently with 30% H_2O_2. This type of catalyst system showed high selectivity and catalytic activity. These considerations prompted us to develop new catalytic oxidation system containing the acidic ionic liquid, low capital cost metal salt sodium tungstate dehydrate ($Na_2WO_4.2H_2O$), hydrogen peroxide and phase transfer catalyst for desulfurization reactions.

Preparation of Acidic Ionic Liquids

Acidicionicliquids:1-(3-sulfonicacid)propyl-3-methylimidazoliumhydrogensulfate([$(CH_2)_3SO_3HMIm$][HSO_4]),1-(3-sulfonicacid)propyl-3-methylimidazoliumtetrafluoroborate([$(CH_2)_3SO_3HMIm$][BF_4]),1-(3-sulfonicacid)propyl-3-methylimidazoliumdihydrogenphosphate([$(CH_2)_3SO_3HMIm$][H_2PO_4]) ,N-(3-sulfonicacid)propyltriethylammoniumtetrafluoroborate[$(CH_2)_3SO_3HTEA$]BF_4,N-(3-sulfonicacid)propyltriethylammoniumhydrogensulfate[$(CH_2)_3SO_3HTEA$][HSO_4],N-(3-sulfonicacid)propyltriethylammoniumdihydrogenphosphate[$(CH_2)_3SO_3HTEA$][H_2PO_4],1-(3-sulfonicacid)propylpyridiniumtetrafluoroborate[$(CH_2)_3SO_3HPy$]BF_4,1-(3-sulfonicacid)propylpyridiniumhydrogensulfate,[$(CH_2)_3SO_3HPy$][HSO_4],1-(3-sulfonicacid)propylpyridiniumdihydrogenphosp

hate[$(CH_2)_3SO_3HPy$][H_2PO_4] were synthesized and purified according to the procedures reported in the literature with a little modified(**Cole, Jensen et al. 2002**).

General procedure of Oxidation of Model Oils

The catalytic oxidative desulfurization experiments of the model oil were carried out in a 50 ml round-bottomed flask with three necks. The required amounts of acidic ionic liquid, catalyst, model oil (1000 ppm sulfur as DBT in normal n-octane) and 30 wt% H_2O_2 were added to the flask in turns, the mixture was stirred vigorously for 3 h in oil bath at reaction temperature. With the same experimental method, the desulfurization experiments were carried out under other conditions. After the reaction, the upper phase (model oil) was withdrawn at room temperature and analyzed by gas chromatography (Nanjing renhuaGC7890A) with tetradecane as internal standard, coupled with a flame ionization detector (GC-FID). AC5 capillary column (30 m×0.53mm inner diameter×1.0μm film thickness) was used for separation. The conversion of DBT in the model oil was used to calculate the removal of sulfur compounds.

Results and Discussion

Influence of Different Reaction Systems

Table 1 shows different desulfurization systems, such as: extraction, extraction coupled with chemical oxidation, extraction coupled with catalytic oxidation in the conditions of the phase transfer catalyst, catalytic oxidation without acidic ionic liquid extraction and catalytic oxidation with acidic ionic liquid extraction without PTC. When using acidic ionic liquid $(CH_2)_3SO_3HMIm$]BF_4 solely as the extractant for removing DBT-containing model oil, the sulfur removal only reached 16.4%, With addition of H_2O_2 in [$(CH_2)_3SO_3HMIm$]BF_4 the sulfur removal increase to 33.8%, continue to add $Na_2WO_4.2H_2O$ the sulfur removal is 63.6%. When catalyst, H_2O_2, the phase transfer catalyst and acidic ionic liquid were employed together, the removal of DBT increased sharply. However, the catalytic oxidation desulfurization system containing $Na_2WO_4.2H_2O$ and H_2O_2 without acidic ionic liquid and PTC, removal of DBT only reached 4.5% and 30.2% respectively. This is because of the precatalyst of $Na_2WO_4.2H_2O$ was oxidized by H_2O_2 to form peroxotungstic species $Na_2[WO(O_2)_2(OH)_2]$, which located in the bottom of the reactor, leading to low sulfur removal. When introduce acidic ionic liquid and phase transfer catalyst the sulfur removal increase substantially. It is really due to the peroxotungstic species $Na_2[WO(O_2)_2(OH)_2]$ accelerated oxidation of DBT aided by the phase transfer catalyst. The results demonstrated that acidic ionic liquid and phase transfer catalyst played an important role in removal of DBT of model oil in the desulfurization system. It can be concluded that acidic ionic liquid not only served as reaction media but also improved the catalytic activity of $Na_2WO_4.2H_2O$ supported by the PTC. Similar results were also found in other acidic ionic liquids.

Influence of Temperature and different phase transfer catalyst on the Sulfur Removal

To investigate the effect of the different phase transfer catalysts and reaction temperature on the oxidative properties, According to the above experimental results it is difficult to achieve deep sulfur levels (<10ppm) without phase transfer catalysts.

Because of reactions with H_2O_2 always involved two phases, which more or less inhibited the reactivity of oxidative desulfurization. For this reason, in this work, it can be introduced a series of amphiphilic quaternary ammoniumsalts such as: tetrabutylammoniumbromide (TBAB), dodecyltrimethylammoniumbromide (DDTMAB), tetradecyltrimethylammonium bromide (TDTMAB), and cetyltrimethylammonium bromide (CTMAB). The catalytic performance of different phase transfer catalyst on the removal of DBT at different temperatures are given in Table 2. As the temperature increased from 30℃ to 60℃, the removal of DBT from the model oil increased respectively . Moreover, the results displayed that the reaction activity decreased as the temperature reached to 70℃. It was because that more H_2O_2 decomposed with the increasing temperature. From the Table 2, it is also concluded that desulfurization degree is decided by the number of carbon atoms of an ammonium cation and sterically hindered(**Zhao, Ren et al. 2007**). The results shown that the desulfurization system contains DDTMAB could reach almost 100%.

Influence of the Amount of H_2O_2 on the Sulfur Removal

To investigate the influence of the amount of oxidizing agent (H_2O_2) on removal of model oil different H_2O_2/sulfur (O/S) molar ratios were carried out at 60℃. According to the stoichiometric reaction, 2 mol of H_2O_2 are consumed for 1 mol of sulfur compound. It was noteworthy that there was a competition between the hydrogen peroxide decomposition side reaction and DBT oxidation reaction. The sulfur removal of different molar ratios of H_2O_2 and DBT are shown in Figure 1.Sulfue removal of model oil increased monotonically with increasing H_2O_2/DBT (O/S) molar ratio, these results also indicated the optimal O/S molar ratio was 4 at 60℃.

Influence of the Amount of Catalyst on the Sulfur Removal

To investigate the influence of the different dosage of catalyst on the sulfur removal, Figure 2 displays the removal of DBT in n-octane vs amount of catalyst. DBT/catalyst molar ratios of 60: 1, 40: 1, 20: 1 and 10: 1 were plotted. As can be seen, increasing the amount of $Na_2WO_4 \cdot 2H_2O$ in the acidic ionic liquid resulted in an increase of S-removal. When the DBT/catalyst molar proportion was changed from 60: 1 to 10: 1, sulfur removal increase from 31.8% to 67.6% at 60℃. In other words, the sulfur removal increased with increasing catalyst dosage. However when desulfurization contains PTC, the S-removal increased sharply, reaching 74.2% to 99.9%, ultra-deep desulfurization can be achieved. It indicated that the amount of catalyst and phase transfer catalyst played an important effect on DBT removal.

The amount of acidic ionic liquid on Sulfur Removal

To investigate the amount of acidic ionic liquid on the sulfur removal, as show in Figure 3, the amount of acidic ionic liquid has a strong influence on the reaction, with the amount of acidic ionic liquid is 0 ml removal of DBT only reached 30.2%, when the amount of acidic ionic liquid is equal or greater than 1 ml, the sulfur compound of model oil can be completely removed. Considering the commercial capital expenditure the amount of acidic ionic liquid is equal to 1 ml, which was chosen in most cases in the present study.

Recovery/regeneration of ionic liquids

After reaction, the reaction system was still a biphasic system in which the acidic ionic liquid phase, along with the catalyst and H_2O_2, were still the lower layer, so the oil could be separated by decantation from biphasic system of the acidic ionic liquid easily. The excess H_2O_2 and model oil were then evaporated from the acidic ionic liquid phase at 120℃ in oil bath for 2 h. Fresh H_2O_2 and model oil then were added into the reaction system for the next run. From the results in Figure 4 indicate that the catalytic system could be recycled five times without obviously decrease in activity.

Mutual solubility of acidic ionic liquid and n-octane

Due to a noticeable mutual solubility of a nitrogen-bearing acidic ionic liquid and n-octane could lead to NO_x pollution and separation cost. So it is important to investigate the mutual solubility between the acidic ionic liquid and the oil in the desulfurization system. By analyzing the acidic ionic liquid-saturated oil sample (acidic ionic liquid was stirred with n-octane) with Elementary analyses. No nitrogen element was found in the sample of acidic ionic liquid-saturated n-octane, which was a proof that ionic liquid has negligible solubility in model oil. The solubility of n-octane in acidic ionic liquid was measured using gravimetric method by weighing the mass of acidic ionic liquid saturated with oil before and after n-octane removal by vaporization at high temperature. The solubility of oil in acidic ionic liquid at room temperature can be overcome by back extraction with water, since acidic ionic liquids are highly hydrophilic. Hence, the problem of the mutual solubility between the acidic ionic liquid and model oil could be avoided.

The Supposed Process and Mechanism of desulfurization System

DBT was chosen as the sulfur compound to research the supposed mechanism of oxidation desulfurization system shown in the Scheme 1(Noyori, Aoki et al. 2003). In acidic ionic liquid phase, $Na_2WO_4.2H_2O$ was almost not dissolved in acidic ionic liquid (Figure5a), When H_2O_2 was added, the catalyst precursor $Na_2WO_4.2H_2O$ is rapidly oxidized by H_2O_2 (Figure5b).The resulting bisperoxotungstate compound A is equilibrium with B and C. Since the pK_a value of C is 0.1, the mono-proton species B is dominant under the acidic ionic liquid phase(Noyori, Aoki et al. 2003), where the acidic ionic liquid forms a great deal of ions of hydrogen, under such acidic conditions, B exists mostly as a monomer. Its anion moiety can easily be transferred to an oil phase by Na+-Q+ ion exchange (Figure5c). Thus, in the oil layer, the bisperoxo complex D undergoes water-DBT ligand exchange to form E. Then proton transfer in E generates the reactive species F, which forms a $DBTO_2$ product and G. The monoperoxo tungstate ion in G is reoxidized by H_2O_2 after returning to the acidic ionic liquid phase as the ion pair H. This step may also occur at an oil–acidic ionic liquid interface or even in the oil phase to some extent (Figure5c). The $DBTO_2$, whose polarity was high enough to be extracted into acidic ionic liquid continuously and accumulated in acidic ionic liquid, which could be easily separated from acidic ionic liquid by centrifugation, Due to the excess H_2O_2 a circulatory system is form; in addition, the sulfur-containing compounds in the model oil were extracted into acidic ionic liquid phase and oxidized to their corresponding sulfones by the peroxotungstic compound in the acidic ionic liquid phase. According to the above processing mode, the deep desulfurization can be achieved.

Conclusions

In this work, the commercially available $Na_2WO_4.2H_2O$ used as catalyst combined with phase transfer catalyst in the acidic ionic liquid is effective for removing DBT of model oil with H_2O_2 as oxidation. Under the optimal conditions, the sulfur removal can reach 99. 9%. Compared with the simple extraction with acidic ionic liquid and catalytic oxidation without ionic liquid and phase transfer catalyst, the process has incomparable superiority. Moreover, this desulfurization system could be recycled five times by distillation without obviously decrease in activity. Meanwhile, the mechanism of oxidation desulfurization was also elaborated.

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