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Deep Desulfurization of Transportation Fuels by Characteristic Reaction Resided in Adsorbents

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A method for deep desulfurization of transportation fuels was presented. Reactive conversion of sulfur compounds and the following adsorption occurred inside adsorbents. The condensation reaction with formaldehyde catalyzed by phosphomolybdic acid was shown effective for the removal of thiophenic and benzothiophenic compounds. Thiophene or benzothiophene of model fuels was completely removed. Coupling with an oxidation reaction, the total sulfur content of commercial fuels was dropped to below 15 ppm. Appropriate desulfur condition was at 70–80°C and ambient pressure without consumption of hydrogen. Saturated adsorbent was regenerated with heating in air at 400°C, and the sulfur capacity was almost fully recovered. Fuel quality was not negatively affected by the desulfur operation. © 2009 American Institute of Chemical Engineers *AIChE J,* 55: 1872–1881, 2009

Keywords: deep desulfurization, transportation fuels, condensation, formaldehyde, phosphomolybdic acid, reaction, adsorption

Introduction

Burning sulfur-laden transportation fuels causes serious pollution in the large cities' air no matter what standard the vehicle technology has been matched. The combustion products of sulfur-laden fuels poison the exhaust conversion catalyst and invalidate the catalyst box. As results, the vehicle emission gets worse and worse irrespective of the advance of autotechnology. Some sulfur compounds converted to sulfates after combustion and emitted into the atmosphere in the form of superfine particles. Suspension of the superfine particles and the inefficiently converted hydrocarbons in the air yields misty and foggy atmosphere. Stringent regulations on sulfur content of transportation fuels have been issued in developed countries presently. For example, it must be lower than 15 ppm by 2007 in the United States. Therefore, the task of deep desulfurization of transportation fuels has drawn global research attention. Thiophene and its derivatives are the species difficultly to remove from fuels and, therefore, the deep desulfurization research is targeting at the removal of this kind of sulfur compounds.

The present state of deep desulfurization technology was extensively reviewed in literature.[1–4] Hydrodesulfurization is the technology practically applied. Most sulfur compounds, such as thiols, sulfides, disulfides, and considerable portion of thiophenes were removed in hydrodesulfurization. However, some benzothiophenic compounds, such as dibenzothiophenes and 4,6-dimethyldibenzothiophene (4,6-DMDBT), still remained in fuels after hydrodesulfurization. Hydrodesulfurization is not a dependable technology for the target of 10 ppm or lower sulfur content. Because of saturation of double bonds for olefin and/or aromatic components,

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excessive hydrodesulfurization of gasoline leads to decrease of octane number. The effectiveness of hydrodesulfurization for diesel decreases either following the increase of aromatic rings or it may further decrease due to existence of aromatic compounds and nitrides. In addition, deep hydrodesulfurization of diesels subject to constraints on fuel density, cetane number, and operation cost. Meanwhile, the catalytic activity decreases as a result of catalyst coking in deep hydrodesulfurization.[5,6] The other desulfurization technologies reported in literature provide more possibilities for deep desulfurization. However, further development is needed for most of them before commercialization. These methods include oxidation, extraction, adsorption, alkylation, and biodesulfurization. Adsorption and oxidation (oxidation–adsorption or oxidation–extraction) are considered promising among them for industrial application. The oxidation method changes the sulfur compounds to sulfones or sulfoxides, and then the polarity difference with other components is utilized in a subsequent treatment. Different techniques were proposed for oxidation method.[7–9] Catalysts are usually used in oxidation, and organic acids,[10,11] heteropoly acids and their salts,[12,13] and Ti-silica molecular sieve[14] were the reported catalysts. The oxidant used includes 30% aqueous hydrogen peroxide,[10,11,13,14] nitrogen dioxide,[15] oxygen,[16] and air.[17] Polar organic solvents or ionic liquids were used as extractant.[18] The oxidation desulfurization method bears merits in mild operation condition and without the expense of hydrogen. However, this method becomes disabled in fuels containing too much aromatic components and/or dissolved water.

Adsorption method can be applied with or without hydrogenation, and the latter is classified into physical or chemical adsorption. The S-Zorb SRT (Sulfur Removal Technology)[19] is a representative of the hydrogenation-based adsorptive desulfurization techniques. Although the method bears merits in less loss of octane number and relatively high desulfurization efficiency, it is not a cost efficient technology because all fuel has to be gasified and reacted at 380–420°C. The desulfurization method basing on physical adsorption seems not to have application potential due to its low selectivity for thiophenic compounds. Prominent success was reported in the method of chemical adsorption, and the IRVAD (Irvine Robert Varraveto Adsorption Desulfurization) method,[20] the π-complexion method,[21,22] and the SARS (selective adsorption for removing sulphur) method[23] are well-known representatives. The IRVAD method is suitable for many liquid hydrocarbons and more than 90% sulfur can be removed. However, the sulfur capacity of adsorbent is low and the adsorbent needs to be frequently regenerated. The sulfur capacity of adsorbent was considerably increased relying on π-complexion. However, the adsorption performance greatly declines where aromatic compounds, oxidants, and moisture are present in fuels.[24] The SARS method[4,23] preloads transition metals on an adsorbent, for example, Ni/SiO_2-Al_2O_3, and reached the same or little higher sulfur capacity compared with the π-complexion method. The alkylation method is to increase the boiling point of sulfur compounds through alkylation reaction and separate sulfur via a subsequent operation. This kind of methods is limited by competitive reaction of aromatic components and the polymerization of olefins.[25] Biodesulfurization might have industrial potential; yet, a lot of fundamental developments are required for a better industrial performance.[2,26,27]

The proposed method relies on adsorbents; however, the desulfur function is not due to adsorption of sulfur compounds, but to the conversion of them via a characteristic reaction occurring in adsorbents. The condensation reaction with formaldehyde (FA) is characteristic for the removal of thiophenic and benzothiophenic compounds. This reaction needs a strong acid as catalyst, and phosphomolebdic acid was applied in the present study. There may be multichoices for adsorbent in practice; however, a silica material with orderly structure SBA-15 was selected in the study for the convenience of examining changes in microscopic structure after loading reagents. Because more sulfur compounds than thiophenic or benzothioiphenic contained in real fuels, the fuel cannot reach the target of deep desulfurization relying only on the condensation reaction. Therefore, oxidation was used as a succeeding reaction after removing thiophens. However, the sulfur load became much less and the effectiveness of oxidation increased considerably.

Why does the characteristic reaction reside in adsorbents? First of all, it aims to increase the selectivity of adsorbent for sulfur compounds; second, because the concentration of sulfur compounds is too low to have the reaction occurred in bulk fuel, though the content of hundreds or thousands ppm is too high to be tolerant. When excessive quantity of catalyst and reagent was preloaded in pore space of adsorbents, sulfur compound will change to another species of larger molecular weight or different property and be adsorbed there as soon as it touches a pore. The large specific surface area/pore volume of adsorbents greatly increased the probability of the touch. Finally, because the reaction occurs in a space/reactor of nanometers dimension, the catalytic activity must increase due to the nanometer's scale of reactors.[28]

Experimental and Method

Preparation of adsorbent/reactor

SBA-15 provided the support of the characteristic reaction and the adsorbent of the reaction products. Details of synthesis and structural property of the SBA-15 were previously reported.[29] Catalyst [phosphomolybdic acid (PMA)] and reagent FA were loaded in SBA-15 before desulfurization. The SBA-15 sample of particular size 0.154–0.180 mm was dipped in 8 wt % water solution of PMA for 1 h under agitation. The sample was dried at 100°C for 12 h followed by vacuum drying at 120°C for 5 h. Then the sample was filled in a column, and the FA vapor carried by a nitrogen stream passed through the column at room temperature and FA was there adsorbed. The weight ratio of PMA/FA/SBA-15 is 0.7/0.4/1.0.

Structure change and loading state of PMA on the SBA-15 sample were examined with different means. ESEM (Environmental Scanning Electron Microscope, XL30, Phlilps, Netherlands), FETEM (Field Emission Transmission Electron Microscope, Tecnai G2 F20, Phlilps, Netherlands), IR (Infrared Spectrometer, FTS3000, BIO-RAD, United States), XRD (X-ray Diffractometer, Rigaku D/max 2500v/pc, Rigaku, Japan) analyses, and adsorption/desorption of N_2 at -196°C were taken.

Testing fuels and chemicals

Desulfurization performance of the sorbent was studied, first with model fuels and then tested in commercial fuels bought from a Sinopec gas station in Tianjin, China. Considering the reactivity difference of different hydrocarbons, three types of model fuels were prepared. Octane was used to represent the aliphatic fuel (ARF) and benzene to represent the aromatic fuel (ALF). A mixture of 80 wt % octane and 20 wt % benzene to represent the mixed type fuels (MXF). As thiophenes and benzothiophenes constituted the obstacle of deep desulfurization, thiophene of 2000 ppm (equivalent to 760 ppm of sulfur element) and 4,6-DMDBT of 1000 ppm (equivalent to 151 ppm of sulfur element) were used to represent sulfur compounds. The total sulfur content in the samples of Sinopec gasoline #93 is 480 ppm and that in diesel #0 is 1300 ppm.

The sulfur content of thiophene in model fuels was detected by GC4000 gas chromatograph equipped with an EC-5 capillary column (length = 40 m, i.d. = 0.32 μm) and a flame photometric detector. The column temperature was set at 60°C and a split ratio of 50/1 was used for the analysis. The temperature of sample gasification was 220°C and the sample size was 2 μl. The minimum detectable sulfur content was about 1 ppm. The sulfur content in the model fuels loading 4,6-DMDBT and in commercial fuels were determined with a coulometric detector Model WK-2D. Calibration curves were prepared before analyses using samples of known sulfur concentration.

Thiophene of analysis grade was purchased from Guangfu Institute of Refinery Chemicals (Tianjin), and 4,6-DMDBT of analysis grade was purchased from J & K Chemical (Beijing). Benzene and *n*-octane of chromatography grade were purchased from Kemiou Chemicals Center (Tianjin). PMA of analysis grade was purchased from Kewei Company (Tianjin). Formalin of analysis grade was purchased from Sanhe Chemicals (Yantai). The commercial gasoline #93 and diesel #0 were purchased from a Sinopec gas station of Tianjin, China.

Experiments and calculation

Appropriate desulfurization condition was first searched in batch tests carried out in a flask with temperature control and agitation facilities. Then breakthrough curves were collected in continuous flows through a packing bed at appropriate condition to determine sulfur capacity of sorbents. Details of batch tests were previously described.[30] Dosage in a batch test is 20 g model fuel and 2.1 g sorbent (containing 1.0 g SBA-15 material). Sulfur content of fuel was analyzed every 15 min. The breakthrough experiments were carried out at a constant temperature in a vertical glass column (length 250 mm, diameter 10 mm) filled with the sorbents. The fuel was pumped up by a mini creep pump model BT01-YZ1515 and flowed down through the column at a rate of 0.5 cm^3/min. Breakthrough curves were drawn on plotting the transient sulfur content of fuel vs. the cumulative fuel volume. The transient sulfur content was normalized with the initial sulfur content of feed whereas the cumulative fuel volume was reduced to unit mass of support/adsorbent. The reduced capacity of the sorbent was calculated with following equations:

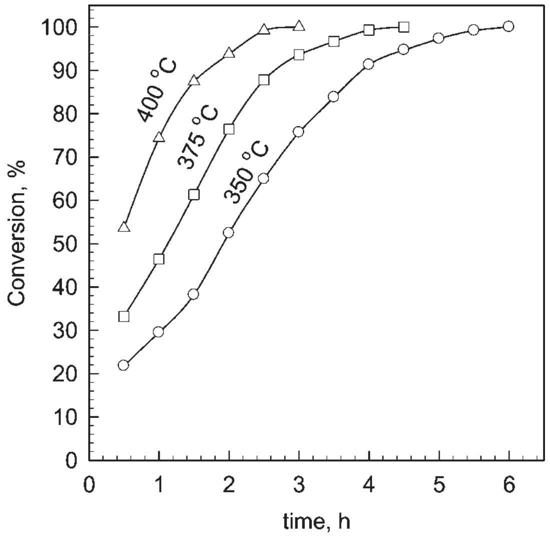


Figure 1. Effect of temperature on regeneration.

$$Q_b = \left(\frac{v\rho x_i}{m}\right) \times t_b \times 100\% \tag{1}$$

$$Q_s = \left(\frac{v\rho x_i}{m}\right) \int_0^{t_s} \left[1 - \frac{c_t}{c_i}\right] dt \times 100\% \tag{2}$$

where Q_b is the breakthrough capacity per unit mass of support (SBA-15), wt %; Q_s is the saturation capacity per unit mass of support, wt %; v is the flow rate of fuel, cm^3/min; ρ is the measured fuel density, g/cm^3; c_i is the initial sulfur content, ppm; c_t is the sulfur content in the effluent fuel at time t, ppm; m is the mass of support packed in the column, g; x_i is the content of sulfur in fuel, wt%; t_b is the breakthrough time, min; and t_s is the saturation time when c_t/c_i=1, min.

Other experiments

Regeneration. The active sites of reaction were gradually covered with the condensation products and saturation capacity was finally shown. Therefore, the reaction products were decomposed periodically. According to the DTA (differential thermal analysis) curve of PMA (not shown), the thermal regeneration temperature was set lower than 430–445°C when the Keggin structure of PMA collapsed. Three temperatures were tested for regeneration, and the result was shown in Figure 1, in which the conversion percentage was based on the sorbent weights before and after regeneration. Thus, 100% conversion means the weight of sorbent after regeneration reduced to the initial weight of fresh sorbent. Compared with lower temperatures, 400°C is preferred. The residual fuel was drawn off before heating sorbent. The saturated sorbent was heated in air at a rate of 5°C/min until 400°C was reached. The temperature of 400°C was maintained for 3 h, and then cooled down to room temperature. The catalyst, PMA, remained in adsorbent after regeneration,

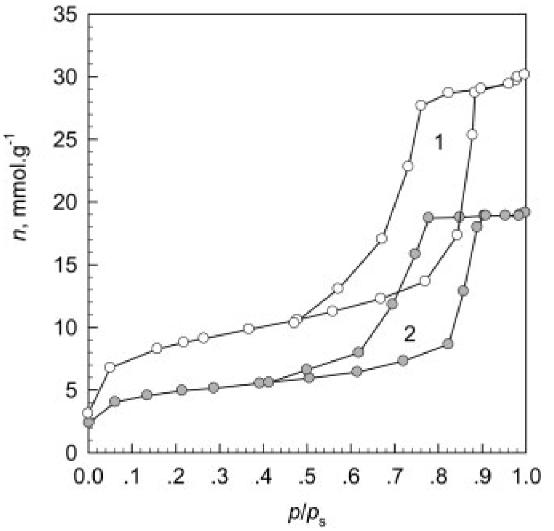


Figure 2. Adsorption/desorption isotherms of N_2 at 77 K on SBA-15 before (Curve 1) and after (Curve 2) loading PMA.

but FA was consumed in reaction and thermal regeneration; therefore, fresh FA was reloaded before completing the regeneration.

Test on Commercial Fuels. In the desulfurization test of commercial fuels, the fuel consecutively passes two beds filling with the sorbent relying on condensation and oxidation, respectively. The oxidation sorbent is made of silica gel (as support/adsorbent) and peracetic acid (as oxidant). The weight ratio of peracetic acid to silica gel was 0.4/1.0. The silica gel has a specific surface area of 315 m^2/g and normal (with the largest distribution probability) pore size of 5.6 nm.

Tests on Corrosion. The corrosion tests include copper corrosion, fuel acidity, and soluble acid of fuels, which were conducted according to the National Standards of China for liquid fuels GB/T258-77 (88), GB/T259-88, and GB/T5096-85 (91), respectively.

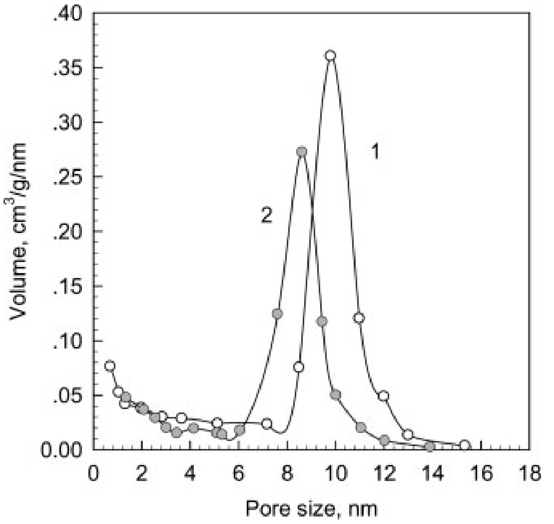


Figure 3. Pore size distribution of SBA-15 samples before (Curve 1) and after (Curve 2) loading 70 wt % PMA.

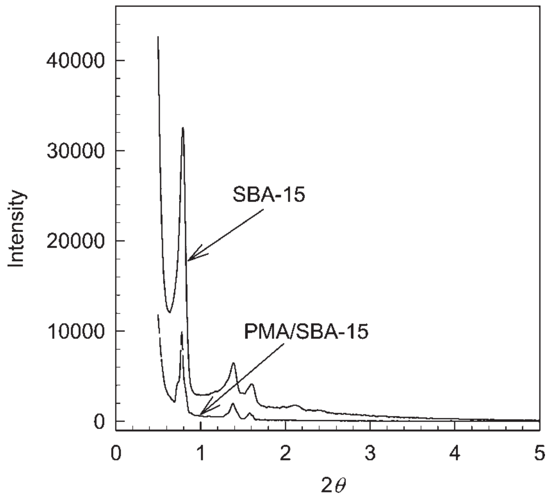


Figure 4. Small-angle XRD pattern of samples.

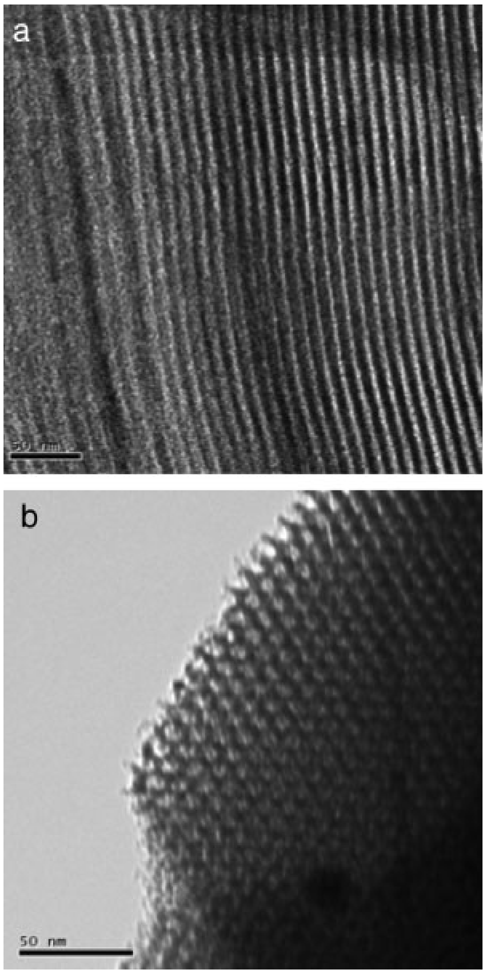


Figure 5. TEM image of PMA/SBA-15.

(a) Electron beam was perpendicular to the channel; (b) electron beam was parallel to the channel.

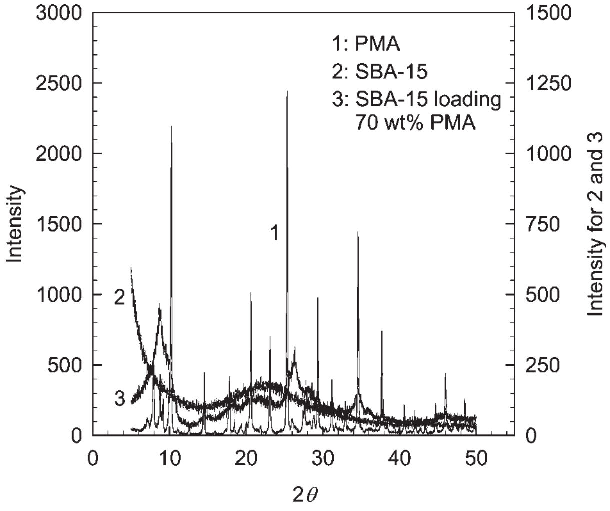


Figure 6. Wide-angle XRD spectrum of samples.

Results and Discussion

Sorbent character

The adsorption/desorption isotherms of N_2 at -196°C are shown in Figure 2 for SBA-15 before and after loading 70 wt % PMA. The feature of Type-IV isotherm remained after loading PMA, though the adsorption amount remarkably decreased. Loading PMA led to decrease in the surface area from 632 to 284 m^2/g and in the pore volume from 0.96 to 0.66 cm^3/g. The surface area and pore volume were evaluated by the α_s-plot method[31] using a macroporous silica gel LiChrospher Si-1000[32] as the reference adsorbent. The surface area was 10.9% larger if BET method[33] was applied. The pore size distribution shown in Figure 3 was determined by the improved KJS method,[34] which adapted the BJH method[35] to the structured mesoporous materials. The PMA/SBA-15 material is still mesoporous, but the nominal pore size reduced from 9.8 to 8.6 nm. This difference is compatible with the molecular size of PMA; therefore, the PMA is basically monolayerly dispersed on the surface of SBA-15.

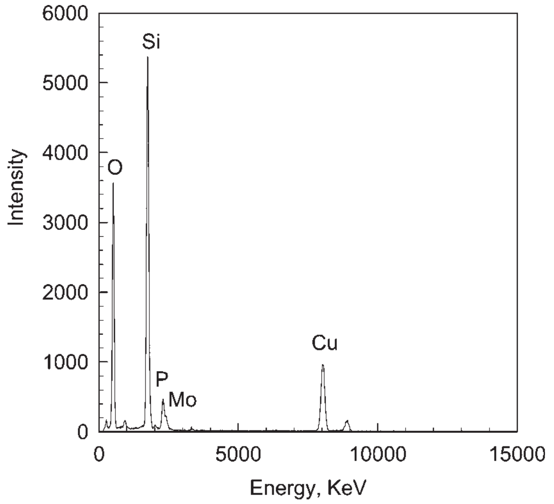


Figure 7. Energy dispersive X-ray spectrum of SBA-15 loading 70 wt % PMA.

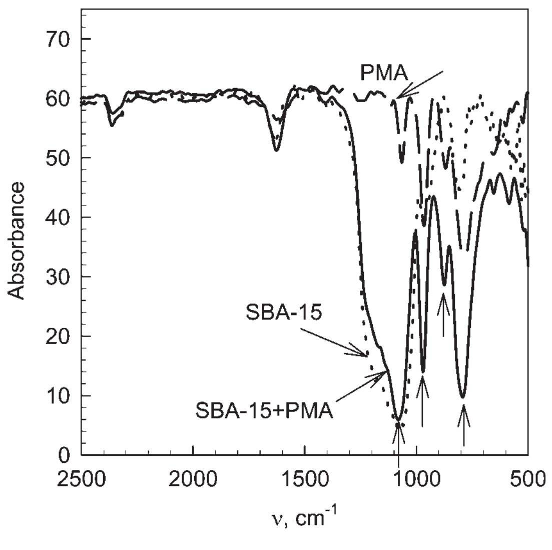


Figure 8. IR spectrum of samples.

The mesoporous structure of PMA/SBA-15 was further supported by the small angle XRD and TEM examinations shown in Figures 4 and 5. The three typical diffraction peaks of SBA-15 indicate existence of the crystal faces (100), (110), (200) after loading PMA, though the intensity decreased. The regular channel structure with mesopore dimension of the pore space rendered the conversion of sulfur compounds controlled by reaction dynamics but not by diffusion. The wide-angle XRD spectrum of samples shown in Figure 6 reflects the secondary structure of the sample. The relatively stronger diffraction peaks in the PMA-loading SBA-15 sample are caused by deposition of some PMA on the exterior surface. The result of EDX (Energy Dispersive X-ray) analysis shown in Figure 7 indicates the existence of

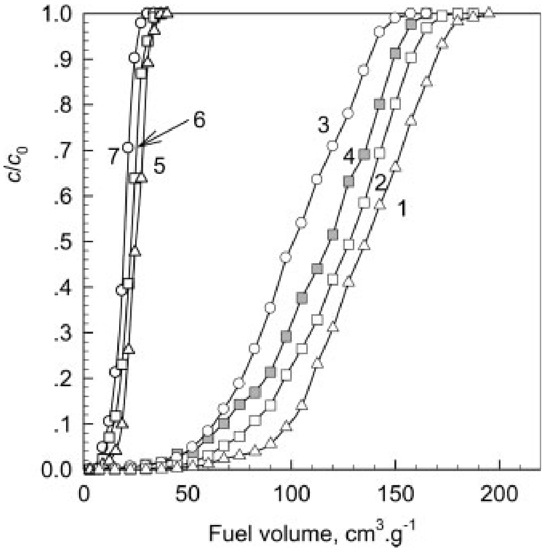


Figure 9. Breakthrough curves of model fuels containing thiophene.

1, 2 and 3: ALF, MXF, and ARF fuel; 4: MXF fuel saturated with dissolved water; 5–7: ALF, MXF, and ARF fuel through the PMA/SBA-15 bed before loading formaldehyde.

Table 1. Sulfur Capacity of Sorbent in Comparison With Other Methods

Desulfur Agent	Thiophene Content (ppm)	Sulfur Content (ppm)	Fuel Type	Q_b (wt %)	Q_s (wt %)
PMA/SBA-15 (without loading HCHO)	2000	760	ALF	0.66	1.37
	2000	760	MXF	0.65	1.29
	2000	760	ARF	0.39	1.18
PMA/SBA-15 (with loading HCHO)	2000	760	ALF	3.74	7.33
	2000	760	MXF	3.05	6.76
	2000	760	ARF	2.54	6.24
	2000	760	H_2O-saturated MXF	2.33	6.57
Yang et al.[22]	2000	760	ALF	5.5	7.54
	2000	760	ARF	0.61	1.73
Dai et al.[30]	2000	760	ALF	6.48	8.52
	2000	760	ARF	1.14	3.92

PMA in the sorbent. The appearance of Cu peak is due to the use of a copper mesh supporting the sample. Infrared (IR) spectrum of the sample mixed with KBr is shown in Figure 8 for the range of 500–2500 cm^{-1}. The four typical absorption peaks at 1063, 961, 871, and 783 cm^{-1} show clearly the Keggin structure of PMA[36] and further indicate the existence of PMA in sorbent.

Desulfur performance in model fuels containing thiophene

Based on batch study, breakthrough curves of different types of model fuels were collected at 70°C over the sorbent bed (Curves 1–4) and shown in Figure 9. Similar curves were also collected when FA was not loaded (Curves 5–7) as a comparison. The breakthrough and saturation capacity for sulfur were calculated based on these curves, and the results are listed in Table 1. Although the sulfur capacity becomes smaller for the fuel rich in aromatic components, the difference is not as large as for the π-complexion method as indicated in the Table. In addition, existence of dissolved water in fuel does not invalidate the desulfur function, though a little decrease in the sulfur capacity was observed. The sulfur capacity was well recovered after regeneration as shown with breakthrough curves in Figure 10. However, some catalyst might lose on regeneration and gradually caused a decrease in capacity. Therefore, some fresh catalyst might be needed a period later.

Desulfur performance in model fuels containing 4,6-DMDBT

4,6-DMDBT is less reactive than thiophene due to the steric hindrance effect. Therefore, its removal was studied in more detail. First, the effect of temperature on the reaction was studied for the range 50–80°C. Although 70°C is appropriate for the removal of thiophene, 80°C is preferred for the removal of 4,6-DMDBT because complete removal was achieved in shorter time as shown in Figure 11. The loading quantity of PMA does not much affect reaction rate for the loading range of 50–90 wt % as shown in Figure 12. Referring to Figure 6, it is argued that loading 50 wt % PMA is enough to match the pore volume of the adsorbent, and excessive load of PMA may yield deposition on the exterior

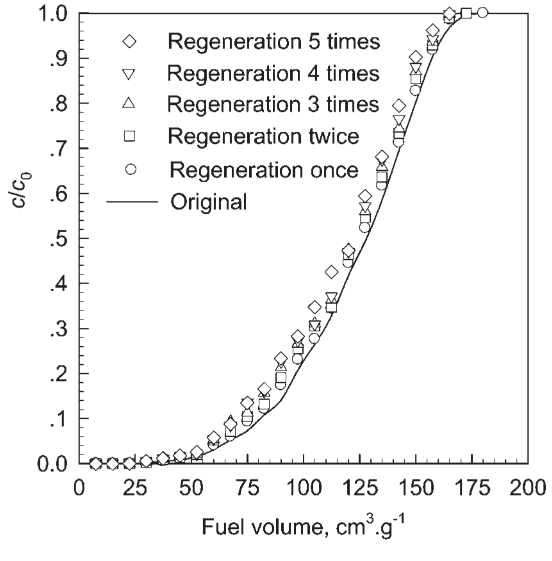


Figure 10. Breakthrough curves of MXF fuel containing thiophene for different times of regeneration.

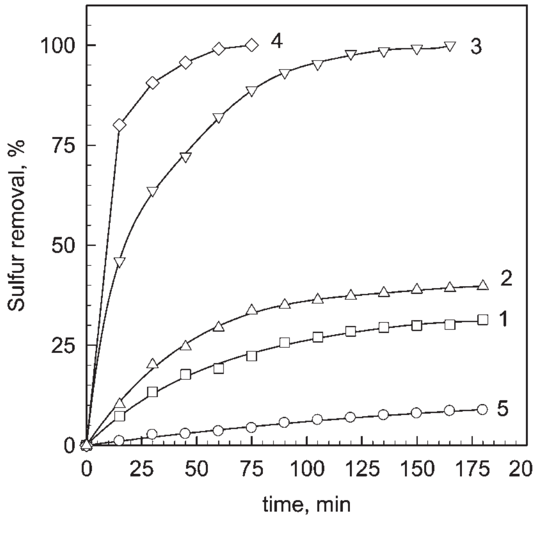


Figure 11. Effect of temperature on the rate of removing 4,6-DMDBT contained in MXF fuel.

1: 50°C; 2: 60°C; 3: 70°C; 4: 80°C; 5: at 80°C without loading formaldehyde.

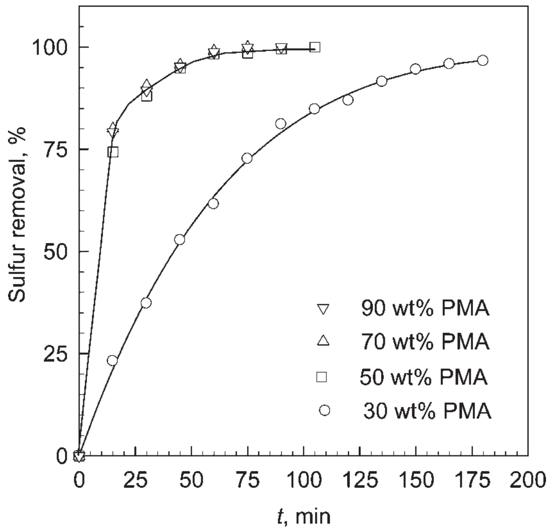


Figure 12. Effect of loading quantity of PMA on reaction rate.

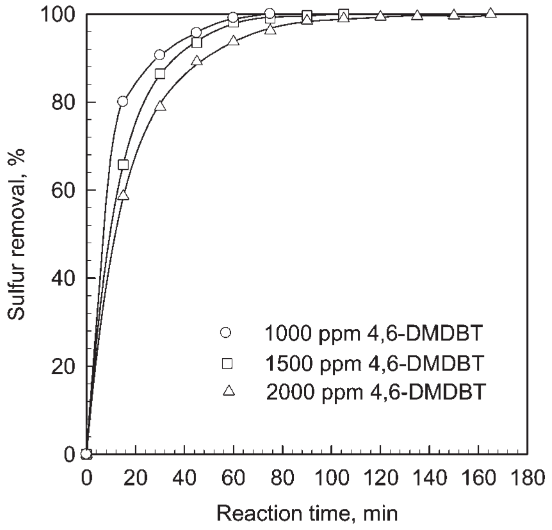


Figure 14. Effect of 4,6-DMDBT amount on reaction rate at 80°C.

surface and does not much contribute to the conversion. However, the reaction rate increases following the increase of FA loading amount from 20 to 40 wt % as shown in Figure 13. The maximal loading amount of FA is limited by the saturation amount of adsorption. Therefore, larger specific pore volume is preferred in selecting adsorbent. Complete removal of 4,6-DMDBT from fuel may take longer time following the increase of its content, but the content of 4,6-DMDBT does not affect much the desulfurization function as shown in Figure 14. Breakthrough curves of different types of fuels containing 1000 ppm of 4,6-DMDBT and passing the sorbent bed at 80°C are shown in Figure 15. These curves look quite similar to those shown in Figure 9, but break the sorbent bed through a little earlier indicating a smaller sulfur capacity in dealing with 4,6-DMDBT. The smaller sulfur capacity is largely attributed to the difference of sulfur percentage in the two molecules: the sulfur element weighs 38.4 wt % in thiophene molecule, but only 15 wt % in 4,6-DMDBT. The sulfur capacity of sorbent can also be recovered after regeneration in dealing with 4,6-DMDBT as shown in Figure 16.

Desulfur performance in commercial fuels

Breakthrough curves were collected using commercial fuels over the sorbent bed as previously done for model fuels, and the results are shown in Figure 17. Two curves are shown for each fuel, one is obtained with fresh sorbent and the other was obtained with regenerated sorbent.

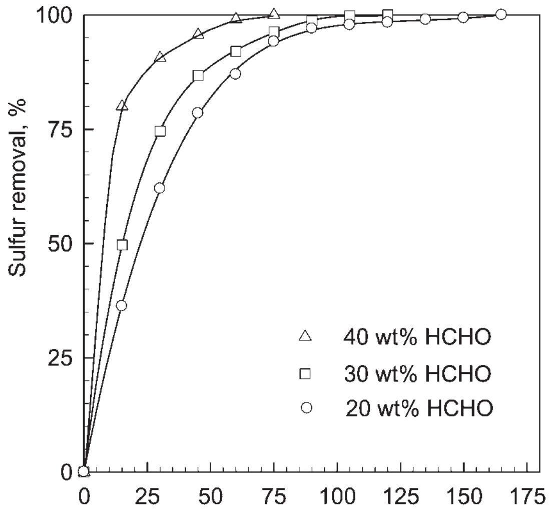


Figure 13. Effect of loading quantity of formaldehyde on reaction rate (loading 70 wt % PMA at 80°C).

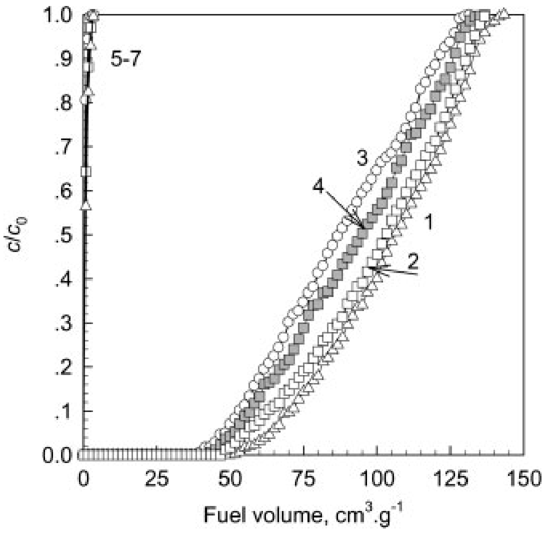


Figure 15. Breakthrough curves of different types of fuels containing 4,6-DBDMT at 80°C.

1, 2, and 3: ALF, MXF, and ARF fuel; 4: MXF fuel saturated with dissolved water; 5–7: ALF, MXF, and ARF fuel through the PMA/SBA-15 bed before loading formaldehyde.

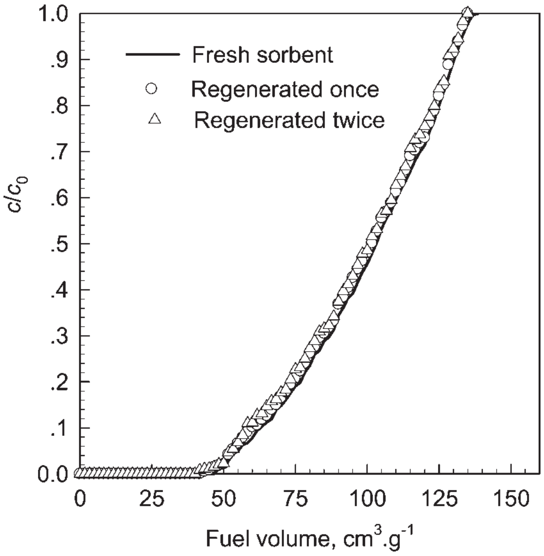


Figure 16. Effect of regeneration on breakthrough curves of MXF fuel containing 4,6-DMDBT at 80°C.

Differently from model fuels, these curves do not start from the origin because some sulfur compounds contained in the commercial fuels do not belong to thiophenic compounds; therefore, cannot be removed by the sorbent relying on condensation reaction. The intercepts indicate how much percentage the other sulfur compounds take part in the given fuel. The total sulfur content in gasoline dropped from 480 to 202 ppm and that in diesel dropped from 1300 to 360 ppm after the first sorption. About 58% sulfur in gasoline and 72% sulfur in diesel belong to thiophenic compounds and were removed by the sorbent relying on condensation reaction. Then the fuel was introduced to another sorbent column. The sorbent consisted of mesoporous silica gel (with BET surface area of 315 m^2/g and normal pore size of 5.6 nm) loading 40 wt % peracetic acid. The total sulfur content in both gasoline and diesel dropped to below 15 ppm after the second sorption. The breakthrough curves of gasoline and diesel consecutively passing through the two sorbent beds are shown in Figure 18. To remove the dissolved water and/or acid in the commercial fuels, 20% volume of the second sorbent (oxidation) bed was filled with blank silica gel.

Corrosion tests were carried out on commercial fuels that experienced two-step sorption following the National Standards of China, and the results are listed in Table 2. Apparently, the desulfur operations did not affect fuel quality.

Discussion on the feature and mechanism of desulfurization

The proposed method for deep desulfurization of transportation fuels possesses three features: The adsorbent has large specific surface area and pore volume; the residence of a characteristic reaction in adsorbents, and the nanodimension of reaction space. The first feature is very important for the success of desulfurization because the concentration of sulfur compounds is very dilute in fuels from the point of view of mass action law, may it be several thousands ppm though. It was shown in experiments that, the condensation reaction did not occur if the catalyst and reagent were directly put in bulk fuel. The large surface/pore of the support/adsorbent radically increased the probability of sulfur species to contact a pore/reactor to trigger the conversion reaction. The residence of characteristic reaction in pore spaces guarantees the selectivity and efficiency of sorbent. The condensation reaction with FA can occur only with thiophenic or benzothiophenic compounds; therefore, olefins or aromatic components of fuels do not interfere with the desulfurization function, which renders the desulfurization function robust and not affecting fuel quality. Without FA, thiophene can occur protonation reaction at elevated temperatures under the catalysis of Brönsted acid as was indicated in literature.[37] The

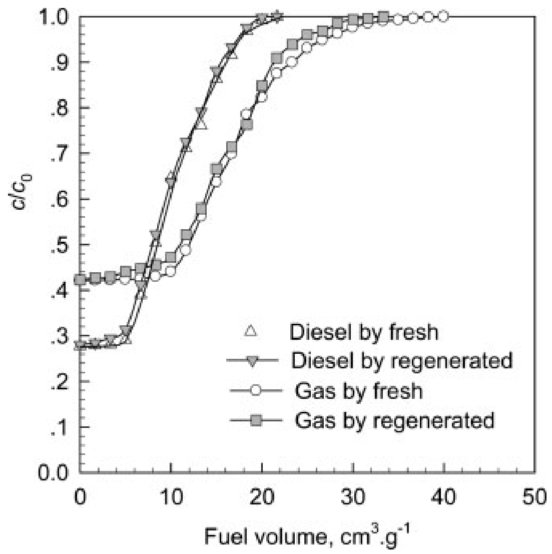


Figure 17. Breakthrough curves of gasoline at 70°C and diesel at 80°C over the sorbent bed.

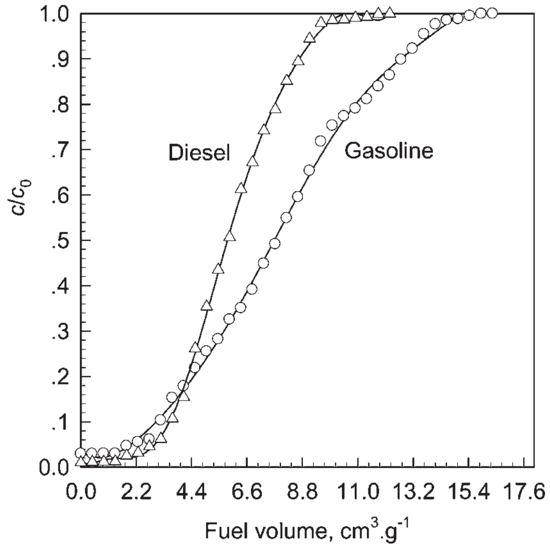


Figure 18. Breakthrough curves of commercial fuels over two consecutive sorption beds (gasoline at 70°C and diesel at 80°C).

Table 2. Result of Corrosion Tests

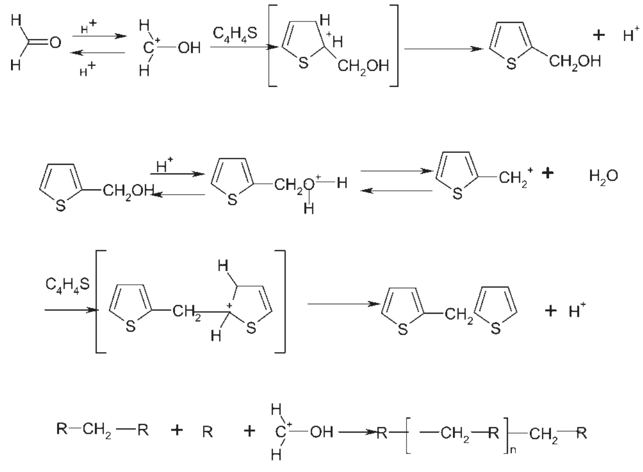
Test	Test Standard	93# Gasoline	0# Diesel	Standard for Gasoline (GB/T 17930-1999)	Standard for Light Diesel (GB 252-2000)
Copper corrosion	GB/T5096-85(91)	1a	1a	Less than Grade 1 at 50°C for 3 h	Less than Grade 1 at 50°C for 3 h
Acidity	GB/T258-77(88)	1.9	2.1	<3	< 7
Soluble acid	GB/T259-88	None	None	None	None

reaction mainly occurs at the α-position of thiophene and triple-thiophene polymers may be formed. However, this reaction is quite weak and only a little sulfur compounds were removed as shown in Figures 9 and 15. The condensation reaction would occur when FA joined, and considerably more sulfur species were removed as proven with Figures 9 and 15. Although different mechanisms were supposed for the condensation reaction, a typical one is shown in Scheme 1.[38] Under the catalysis of strong acid, FA contributes a pair of electrons to H^+ and accepts a pair of electrons of thiophene ring forming a metastable intermediate. The intermediate changes to alcohol following the movement of H^+ and further changes to positive ion of methylthiophene, which accepts a pair of electrons from thiophene ring and replaces the H^+ forming methyldithioiphene and further yielding phenolic resins, i.e., the Novolac-type resins. Nanodimension of the reaction space guaranteed the complete conversion of sulfur compounds. The larger pore volume allows for loading excessive quantity of reagent and catalyst, and the several nanometers scale of pore spaces renders the catalytic activity more active.[28] As a result of polymerization reaction, sulfur element enters the molecule of much larger size and stays in the pore/reactor. A subsequent separation operation of sulfur from fuel is no longer needed. The mesopore dimension of the reaction spaces avoids the effect of diffusion resistance on the reaction dynamics and renders the reaction rate of quasi-first order.

The reaction order can be evaluated from a plot of $\ln[c_0/c]$ vs. reaction time. Such a plot is shown in Figure 19 for the conversion of thiophene at different temperatures. The reaction rates at different temperatures were determined from plot slopes, and activation energy of the desulfurization reaction was then evaluated based on rate constants from an Arrhenius plot. The result was 105.4 kJ/mol for the conversion of 4,6-DMDBT and 73.8 kJ/mol for the conversion of thiophene.

Conclusions

1. The sorbent/reactor relying on condensation with FA and catalyzed by phosphmolybdic acid completely removed thiophenes and benzothiophenes from model fuels. The double bonds of olefins or aromatic components were not affected during desulfurization; therefore, they did not interfere with the desulfurization function either.
2. Together with succeeding oxidation resided in adsorbent, the total sulfur content of commercial fuels dropped to below 15 ppm.
3. Saturated sorbent was easily regenerated and the desulfur operation did not affect fuel quality.
4. The coupled reaction/adsorption function calls for mild operation condition: 70–80°C and ambient pressure without the expense of hydrogen.



Where R=thoiphene and it's homologs having at least two activated ring positions

Scheme 1. Condensation reaction of thoiphene with formaldehyde.

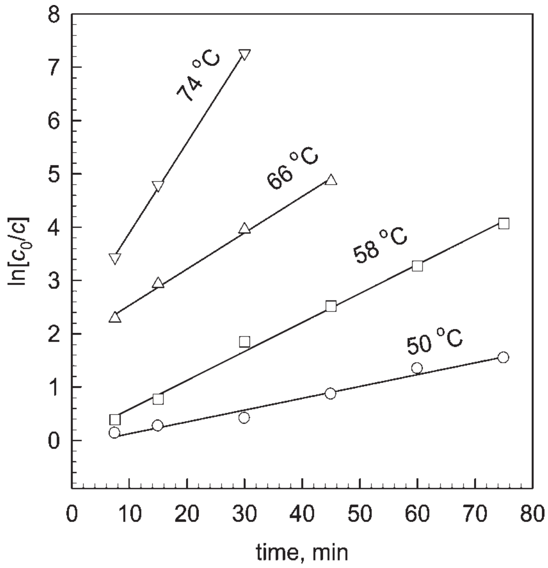


Figure 19. Plot of determining reaction order (for the conversion of thiophene).

5. The reaction resided in adsorbents is promising for industrial application in the separation of dilute species.

Acknowledgements

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