



# Desulfurization from thiophene by $\text{SO}_4^{2-}/\text{ZrO}_2$ catalytic oxidation at room temperature and atmospheric pressure

Bo Wang\*, Jianpeng Zhu, Hongzhu Ma

Institute of Energy Chemistry, College of Chemistry and Materials Science, Shaanxi Normal University, Xi'an 710062, China

## ARTICLE INFO

### Article history:

Received 27 March 2008

Received in revised form 2 August 2008

Accepted 6 August 2008

Available online 13 August 2008

### Keywords:

Desulfurization

$\text{SO}_4^{2-}/\text{ZrO}_2$

Ozone

Thiophene

Sulfur compounds

## ABSTRACT

Thiophene, due to its poison, together with its combustion products which causes air pollution and highly toxic characteristic itself, attracted more and more attention to remove from gasoline and some high concentration systems. As the purpose of achieving the novel method of de-thiophene assisted by  $\text{SO}_4^{2-}/\text{ZrO}_2$  (SZ), three reactions about thiophene in different atmosphere at room temperature and atmospheric pressure were investigated.  $\text{SO}_4^{2-}/\text{ZrO}_2$  catalyst were synthesized and characterized by X-ray photoelectron spectroscopy (XPS), Fourier transformation infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and scanning electron microscope (SEM). The products were detected by gas chromatography–mass spectrometry (GC–MS). XP spectra show that ozone-catalyst system (SZO) have two forms of sulfur element ( $\text{S}^{6+}$  and  $\text{S}^{2-}$ ) on the catalyst surface, which distinguished from that of air-catalyst system (SZA) and blank-catalyst system (SZB) ( $\text{S}^{6+}$ ). And the results of GC–MS exhibited that some new compounds has been produced under this extremely mild condition. Especially, many kinds of sulfur compounds containing oxygen, that is easier to be extracted by oxidative desulfurization (ODS), have been detected in the SZA-1.5 h and SZB-3 h system. In addition, some long chain hydrocarbons have also been detected. While in SZO-0.5 h system, only long chain hydrocarbons were found. The results show that total efficiency of desulfurization from thiophene with ozone near to 100% can be obtained with the  $\text{SO}_4^{2-}/\text{ZrO}_2$  catalytic oxidation reaction.

© 2008 Elsevier B.V. All rights reserved.

## 1. Introduction

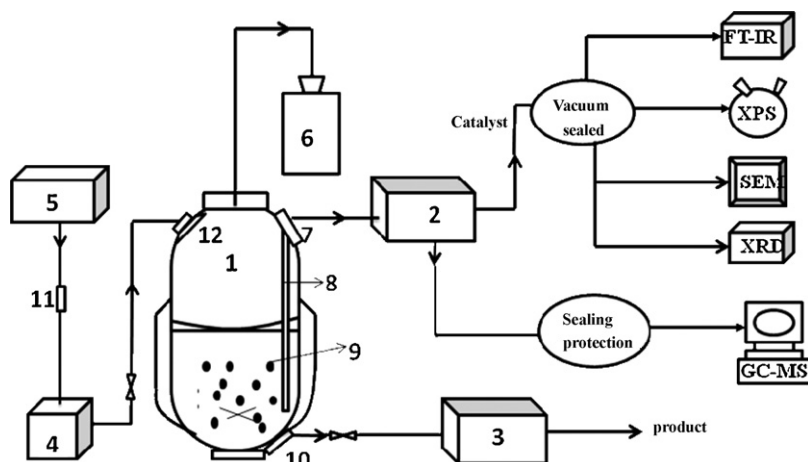
Recently, much more attention has been paid by governments to the desulfurization of gasoline to meet the regulation for environmental protection. The US federal government and European parliament mandated reduction of sulfur levels, which will be reduced to below 10 ppm by the year 2010 [1]. Thiophene, colorless liquid, with pungent odour and highly flammable (boiling point:  $84^\circ\text{C}$ , flash point:  $-1^\circ\text{C}$ ), is an aromatic heterocyclic compound consisting of four carbon atoms and one sulfur atom in a five-membered ring. Its vapour/air mixtures are explosive (explosive limits, vol.% in air: 1.5–12.5). If inhalation and short-term exposure, it would arouse cough, dizziness, sore throat and irritate the eyes and the skin. It can react violently with oxidizing materials, including fuming nitric acid. Thiophene decomposes on heating and burning, producing toxic and irritating fumes (sulfur oxides).  $\text{SO}_x$  species are the direct compounds leading to acid rain [2].

There are several well-established traditional technologies in desulfurization. The hydrodesulfurization (HDS) of gasoline was

carried out at about 623 K and pressure of 2–20 MPa, which are extremely out of mild condition [3,4]. Lots further researches of catalysts related HDS were devised [5]. But the method of HDS is still limited by its high cost. More new selective desulfurization processes and innovative desulfurization approaches, not related to HDS technology, are required urgently. Currently, in order to remove these refractory sulfur compounds from petroleum products, there are many researches and development efforts on alternative methods, such as selective adsorption [6–8], ionic liquid extraction [9], electrochemical oxidation [10], etc. Among these methods, oxidative desulfurization (ODS) is a promising new method [11–13]. ODS selectively oxidize sulfur compounds to sulfioxides or sulfones, which can be extracted by a polar solvent. Sulfur has a strong affinity for oxygen, and oxygen can be added to sulfides and thiophene derivatives without breaking any carbon–carbon bonds. This process has been used effectively to remove sulfur from fuel.

Sulfated metal oxides is a new type of catalyst, it has some advantages, not only for its acid strength ( $H_0 \leq -12$ ) [14], but also no corrosion for the reactor and being free from pollution for the environment. Moreover, this type of catalyst can be widely used in many reactions, such as hydrocarbon transformations, esterification, isomerization of *n*-alkanes, polymerization, acylation, and

\* Corresponding author. Tel.: +86 29 85308442; fax: +86 29 85307774.  
E-mail address: [wangbo@snnu.edu.cn](mailto:wangbo@snnu.edu.cn) (B. Wang).



**Fig. 1.** Schematic diagram of the experiment. (1) Slurry reactor, (2 and 3) separator, (4) dryer, (5) gas generator, (6) gas absorber (NaOH), (7) sample output, (8) sampling pipeline, (9) catalyst, (10) product output, (11) flow meter, (12) gas distribution.

so on [15,16]. Sulfated zirconia ( $\text{SO}_4^{2-}/\text{ZrO}_2$ ) is a typical example and exhibits an excellent catalytic activity for the reactions, has attracted much attention [17,18].

Based on the previous researches on the desulfurization, the reaction of thiophene catalyzed by  $\text{SO}_4^{2-}/\text{ZrO}_2$ , assisted by air or ozone, has been investigated. Compared with the traditional ODS, in this method, it is not necessary to extract the sulfur compounds in ozone-catalyst system (SZO) system. The results suggested that this method can be achieved in oxidative desulfurization of oil and high thiophene concentration systems, such as its vapour/air mixture occasions (vapour should be collected and compressed to liquid before treating). Due to the process operated at room temperature and atmospheric pressure, large cost can be saved. In addition, the liquid products are mostly hydrocarbons, which could be directly combusted without any pollution.

## 2. Experimental

### 2.1. Materials

The chemical reagents used in the experiment were of analytical grade and without further purification.

### 2.2. Catalyst preparation

The sulfated metal oxide ( $\text{SO}_4^{2-}/\text{ZrO}_2$ ) was prepared with chemical co-precipitation method as the following procedures: 100 g of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  was dissolved in distilled water, followed by addition of 25% aqueous ammonia dropwise with stirring, the final pH of the solution was adjusted to 8–9. The hydroxide was thoroughly washed until free from the subsistent chlorine ions which could affect the activity of catalyst, then dried in the air at 373 K for 24 h. Subsequently, sulfate adsorption on the dried zirconia sample was carried out by immersing the zirconia powder in a 0.8 mol/L sulfuric acid solution for 8 h. The sulfated sample was washed and dried in vacuo at 373 K. Finally, calcination of the material was processed at 823 K for 3 h to obtain the catalyst.

### 2.3. Experiment process

Fig. 1 provides a schematic diagram of the experimental equipment used in the slurry reactor operations [19]. Slurry reactor is a kind of three phase fluidized bed which catalyst is fluidized by the flow of liquid slurry (catalyst/reagent wt.% <20%). The gas feed

flow rate was controlled by gas generator <5> (ozone 2.5 g/h) which depended on the gas along with the effluent gas flow from the reactor and was continuous during the run. However, the slurry mixture of thiophene and catalyst powder was batch in operating mode. After the introduction of 50 mL of thiophene solvent and 9 g catalyst powder, the procedure was carried out with the agitator stirring effectively, achieving finely divided catalyst suspended in thiophene. In order to investigate the effect and influence of air and ozone of desulfurization under SZ, three groups of reactions were designed in our lab-styled experiment, including thiophene–ozone system, thiophene–air system, thiophene–off gas system. During these courses, certain content liquid was sampled from sample output <7> every 30 min. Table 1 gives the symbol of samples and catalysts. At the end of the reactions, the products and catalyst were collected from product output <10>. Prior to analysis, the product has been separated and then was analyzed by gas chromatography–mass spectrometry (GC–MS), while the catalyst has been analyzed by scanning electron microscope (SEM), X-ray diffraction (XRD), X-ray photoelectron spectra (XPS), Fourier transformation infrared spectroscopy (FT-IR). A kind of acid gas was detected and absorbed by gas absorber (NaOH) <6>. The color of SZO has converted into gray from white.

### 2.4. Analytical methods

The scanning electron microscope measurements were performed using Quanta 200 scanning electron microscope produced by Philips at 20 kV. The surface composition of catalyst after the reaction was analyzed by X-ray photoelectron spectroscopy using a XSAM800 (Kratos) equipment operated in the FAT mode with the nonmonochromatic Mg X radiation ( $h\nu = 1253.6$  eV). The base pressure in the chamber was in the range of  $10^{-8}$  Pa. Charging of catalyst sample was corrected by setting the binding energy of carbon (C 1s) at 284.6 eV. X-ray diffraction measurements of the catalyst powder were recorded using D/Max-3c (Janpan Rigalcu) diffractometer equipped with Ni filtered Cu  $K\alpha$  ( $\lambda = 1.5406$  Å). Fourier transformation infrared spectroscopy analysis of catalyst was car-

**Table 1**  
Symbol of samples

	0.5 h	1 h	1.5 h	3 h	Catalyst
Ozone	SZO-0.5 h	SZO-1 h	SZO-1.5 h		SZO
Air	SZA-0.5 h	SZA-1 h	SZA-1.5 h		SZA
Blank	SZB-0.5 h	SZB-1 h	SZB-1.5 h	SZB-3 h	SZB

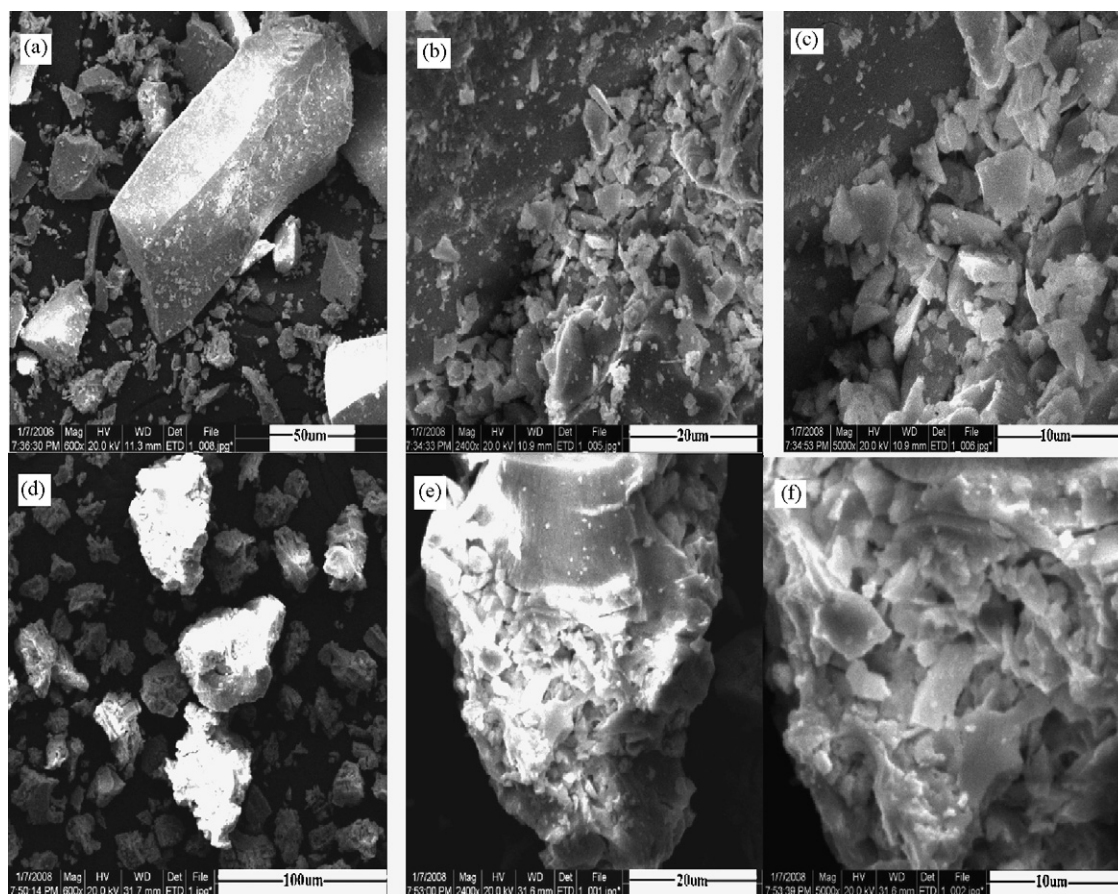


Fig. 2. SEM micrographs of catalysts. SZ for before reaction (a) 600 $\times$ , (b) 2400 $\times$ , and (c) 5000 $\times$ . SZO for after reaction (d) 600 $\times$ , (e) 2400 $\times$ , and (f) 5000 $\times$ .

ried out on a Bruker IFS 28 FT-IR spectrometer equipped with a MCT detector (resolution of 4  $\text{cm}^{-1}$ ). The samples were prepared as self-supporting wafers (2 cm diameter and typically 7–8  $\text{mg}/\text{cm}^2$ ) and were heated under vacuum at 373–773 K for 1 h before recording spectra. FT-IR spectra of 1% (wt.%) catalyst in KBr disk were obtained in the range 4000–400  $\text{cm}^{-1}$ .

The composition of products was analyzed with gas chromatography (HP6890)–mass spectrometry (JMS-600 W, JEOL). The GC–MS condition was as follows: helium carrier gas with a 1.0 mL/min flow rate was used. The effluent from the GC column was directly connected to MS. The mass spectrometer was operated in the positive-electron impact mode with the ionization energy of 70 eV. The identification of each peak was achieved by comparing the retention time (rt) and mass spectra.

### 3. Results and discussion

#### 3.1. Characterization of the catalyst

##### 3.1.1. Scanning electron microscope and BET

The surface morphology of the catalyst before (SZ) and after reaction (SZO) were compared (Fig. 2). It can be seen that the surface of catalyst before reaction was smooth, the size of the catalyst was not uniform and varied from 10 to 100  $\mu\text{m}$  before reaction, however, after reaction the particles are uniform (about 5  $\mu\text{m}$ ), it became rough and looser after reaction, indicating that the surface was changed in the desulfurization process.

All the samples were calcined at 773 K for 1 h in order to obtain comparable BET surfaces. The surface area of the sulfated oxide is

much larger (50  $\text{m}^2 \text{g}^{-1}$ ) than that of the oxide (25  $\text{m}^2 \text{g}^{-1}$ ) without the sulfate treatment, indicating that  $\text{SO}_4^{2-}$  anions on the surface of  $\text{SO}_4^{2-}/\text{ZrO}_2$  can effectively impede its crystallization in calcination, thus hindering the loss of its surface area.

##### 3.1.2. X-ray diffraction

The XRD patterns of catalysts before and after reaction are presented in Fig. 3. It is a known fact in the literature that high-temperature treatment normally leads to sintering of the samples. The powder of SZ sample was calcined at 823 K. Sulfated zirconia crystallize into the tetragonal crystalline phase at temperatures usually higher than 873 K. As can be noted from this figure, the sample (Fig. 3a) exhibits poor crystallinity. Only the broad diffraction

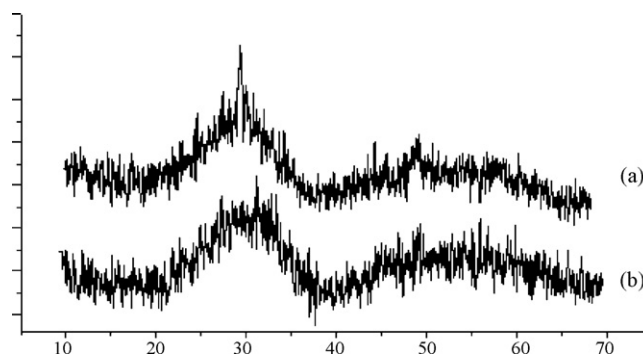


Fig. 3. XRD patterns of SZ (a) and SZO (b).



**Table 2**

Comparison of XPS data for element concentration on the surface of SZB, SZA and SZO

	C 1s	O 1s	Zr 3d	S 2p
<b>SZB</b>				
Area (cts-eV/s)	40,557	31,730	16,193	1266
Concentration (%)	72.18	23.51	3.31	1.00
<b>SZA</b>				
Area (cts-eV/s)	52,525	34,695	14,870	1190
Concentration (%)	75.9	20.87	2.47	0.76
<b>SZO</b>				
Area (cts-eV/s)	59,690	49,155	12,578	2826
Concentration (%)	72.04	24.70	1.74	1.52

lines due to  $ZrO_2$  can be seen. There were little differences in XRD patterns, possibly concluding that a change in phase does not occur in the process of the reaction.

### 3.1.3. X-ray photoelectron spectroscopy

Comparison of the XPS data for element concentration on the surface of blank-catalyst system (SZB), air-catalyst system (SZA), SZO (Table 2), it can be clearly seen that the adsorbed sulfur content in the catalyst were relatively high, which is coincident with the others reported [20]. It also can be found that the sulfur content in SZO was absolutely highest than that of SZA and SZB, moreover, the molar ratio Zr/S of 3.31, 3.25 and 1.15 for SZB, SZA and SZO system respectively, were obtained, indicating that SZO system is more active in adsorbing sulfur species than SZA or SZB system.

The binding energies of Zr 3d5/2 and 3d3/2 (Fig. 4) are in agreement with the values reported in the literature [21]. In SZA and SZB system of Zr spectra, it can be found that these two peaks overlapped without any difference on binding energy, indicating that the chemical environment of Zr were the same in these two catalysts. While for SZO catalyst, the double peaks of 3d5/2 and 3d3/2 shift to a low binding energy, which means the chemical environment of Zr has changed. It may be due to the following reason: the electron cloud density of zirconium was increased when Zr–O bond was substituted by Zr–S bond, which will contribute to the lower binding energy. This hypothesis was also testified by XP spectra of S element.

The S=O structure is essential for generation of acid sites on sulfate promoted oxide samples. The strong ability of S=O in sulfate complexes to accommodate electrons from basic molecules is a driving force for generation of highly acidic properties [22]. In order to determine that  $SO_4^{2-}$  group was successfully integrated, XP spectra of S element were also discussed. The binding energy of S 2p3/2 in these two catalysts (Fig. 5) were observed at 169.20 eV, agreeing with that of  $Zr(SO_4)_2$  [23], indicated that the S element

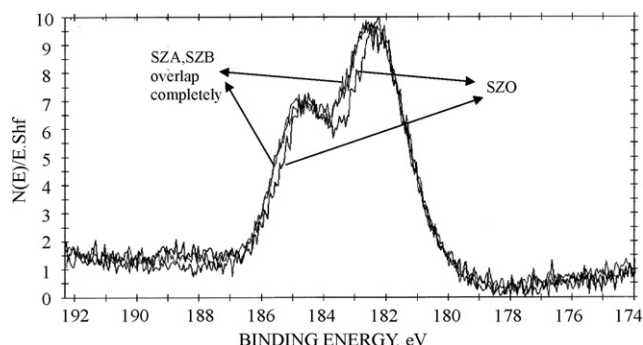


Fig. 4. Binding energy of Zr in SZO, SZA, SZB.

existed in the form of  $S^{6+}$  in the catalysts. The conclusion was also consistent with the FT-IR results.

While the binding energy of S 2p3/2 in SZO (Fig. 5c) not only achieve the peak at about 169.2 eV as that of SZA and SZB, but also the peak of 163.02 eV was located, which absolutely belong to  $S^{2-}$  [24].  $S^{2-}$  ion, transformed rarely from  $S^{6+}$ , may come from the reaction of thiophene with ozone in the presence of catalyst, which was also inferred that the desulfur activity of SZO catalyst was higher than that of SZA and SZB catalyst.

In the XP spectrum for C 1s of SZO, the spin-orbit components of the peak were well-deconvoluted to four curves (Fig. 6 and supplement material Table S1). The peak at 285.89 eV, corresponding to C=C, proved that the presence of unsaturated hydrocarbon formed during the process. The appearance of the lower one at 284.61 eV, corresponding to C–C, was possibly due to the firm adsorption of the reactant or products. Two separate peaks at 288.18 and 286.81 eV, attributed to COOH groups and C=O, respectively [25].

### 3.1.4. FT-IR spectroscopy

Infrared spectra provide the messages of catalyst and its structure. Fig. 7 shows the representative infrared spectra of SZB, SZA and SZO. S exhibits great acid strength, its attribute to existence of  $SO_4^{2-}$  group. In the region 1400–900  $cm^{-1}$ , the spectral pattern observed here is quite complex, which accorded with the sulfate vibrations [26,27]. XP spectra have made sure of that  $S^{6+}$  existed on the surface of catalyst. Two possibilities of the sulfate vibrations of  $SO_4$  groups were observed. One is chelating bidentate structure (Fig. 8a), whereas another vibrations is a bridged bidentate structure (Fig. 8b). For Zr element, it can be determined that binding structure of  $SO_4^{2-}$  to Zr ions exhibits the bridged bidentate form [28]. As the  $SO_4^{2-}$  group existed, due to the strong attracting electrons from Zr ions via two covalent S=O bonds, the centre metal atom lacks electrons severely, thus strong Lewis acidic strength is generated. And at the same time, Lewis acid could converts to Brønsted acid site when Lewis acid site adsorbs water, which shows in Fig. 8c vividly. Sulfation resulted in the appearance at about 1605  $cm^{-1}$ , which was matched with the bending mode of chemisorbed water coordinated to Lewis acid sites oxyhydrogen-bonded to polar sulfate/hydroxyl groups [29,30]. However, band at 1680  $cm^{-1}$  is due to the stretching vibration bands of ketonic double bonds C=O, which may overlap with chemisorbed water [31]. A wide band appears at 3449  $cm^{-1}$  corresponding to OH vibration which is ascribed to the physisorbed water in the catalyst [32].

## 3.2. Characterization of the products

### 3.2.1. GC-MS

Gas chromatography in conjunction with mass spectrometry has been known for its superior separation of complex organic compounds, greater sensitivity and shorter measuring time, hence is better suited for detection and identification of volatile organic compounds.

Fig. 9 and Table 3 show the GC spectrum (MS show from supplement material MS Date S2) and the products distribution of the SZB system 3 h later (SZB-3 h). Five main products were obtained, most are long chain hydrocarbons located (after rt 9 min), accounted for almost 100% selectivity in the products distribution. Long chain hydrocarbon could combust without any pollution for environment. According to MS analysis, little sulfur compounds (a–d) has been detected.

Fig. 10 and Table 4 show the GC spectrum (MS show from supplement material MS Date S2) and the products distribution of SZA system 1.5 h later (SZA-1.5 h). At the different conditions of gas

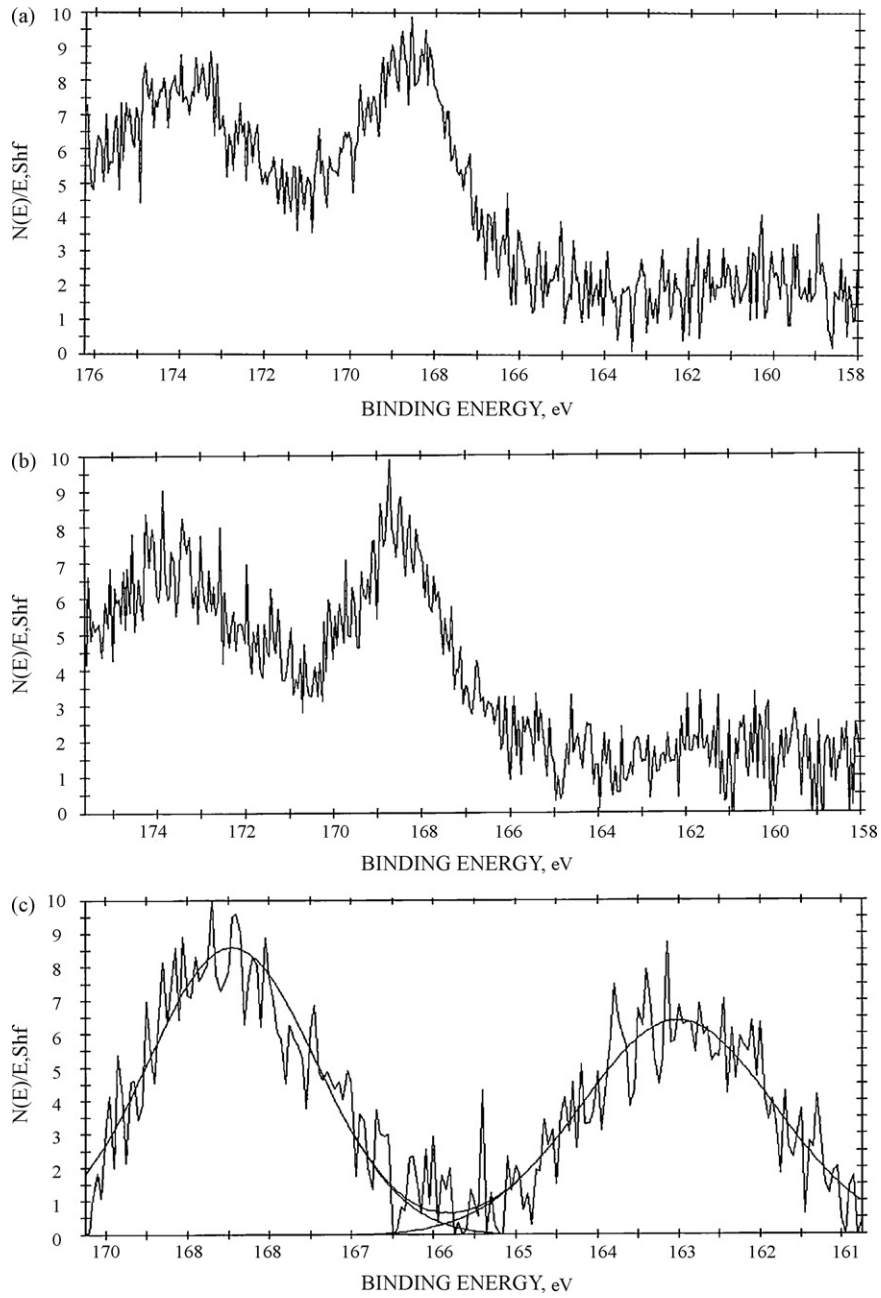


Fig. 5. Binding energy of S 2p3/2 SZB (a), SZA (b) and SZO (c).

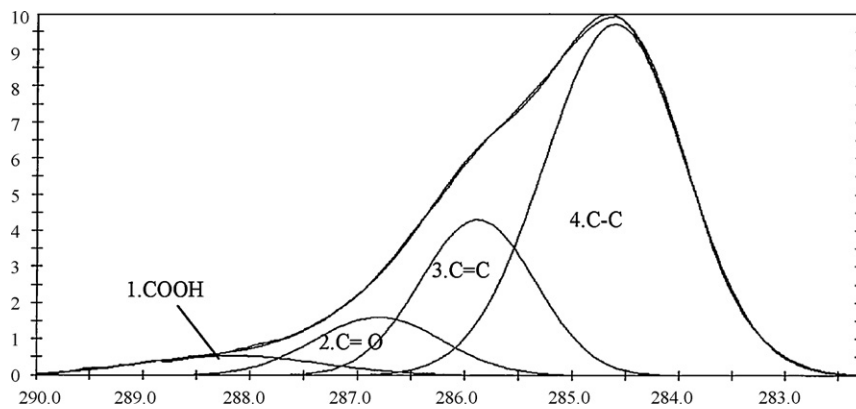


Fig. 6. XPS spectra of C 1s of SZO.

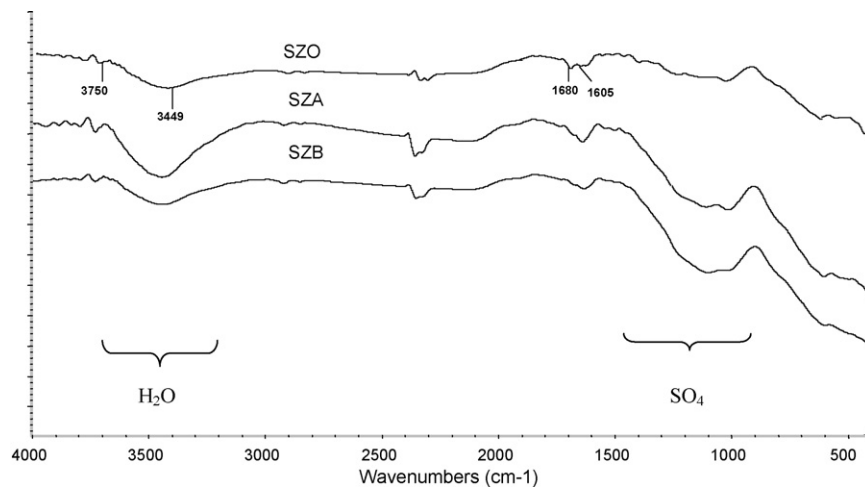


Fig. 7. FT-IR of catalyst.

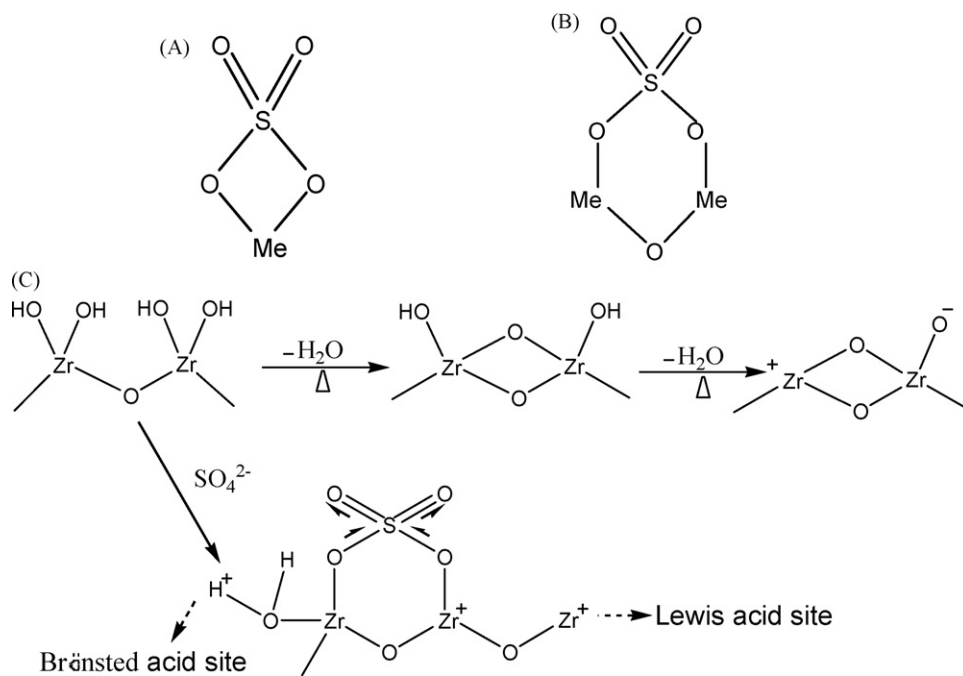


Fig. 8. Binding form of  $\text{SO}_4$  and structure of SZ. (A) Chelating bidentate; (B) bridged bidentate; (C) Lewis acid and Brønsted acid site of the catalyst.

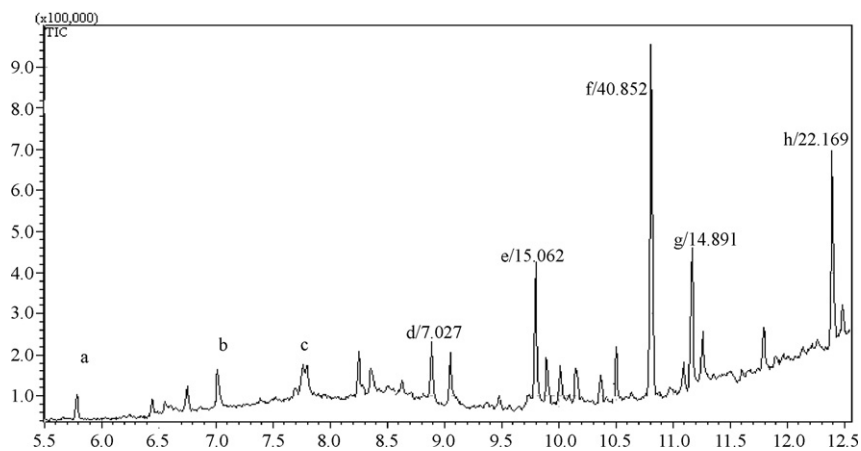


Fig. 9. GC of the product catalyzed by SZB system (SZB-3 h).

**Table 3**  
Product distribution of SZB system (SZB-3 h)

Compounds	Structure	Selectivity (%)
a		Little
b		Little
c		Little
d		7.03
e–h	Hydrocarbon	92.97

and off gas in the two reactions, it can be found that more kinds of product has been formed than that of SZB-3 h, indicating that more efficiency of desulfurization catalytic activity of the catalyst has been achieved during the oxidative desulfurization of thiophene in air.

Fig. 11 and Table 5 show that GC spectrum (MS show from supplement material MS Date S3) and the products distribution of ozone system 0.5 h later (SZO-0.5 h). Compared with SZB-3 h, SZA-1.5 h, only three long chain hydrocarbons have been detected. Sulfur element has been converted into a kind of acid gases, indicated that the efficiency of desulfurization is higher than that of SZB-3 h, SZA-1.5 h. It is more simple to remove the sulfur element from certain system than the traditional ODS method at room temperature and atmospheric pressure. In order to prove this assumption, the effect of time on the desulfurization of thiophene reaction, was also investigated. The same result has been obtained: no sulfur

**Table 5**  
Product distribution of SZO system (SZO-0.5 h)

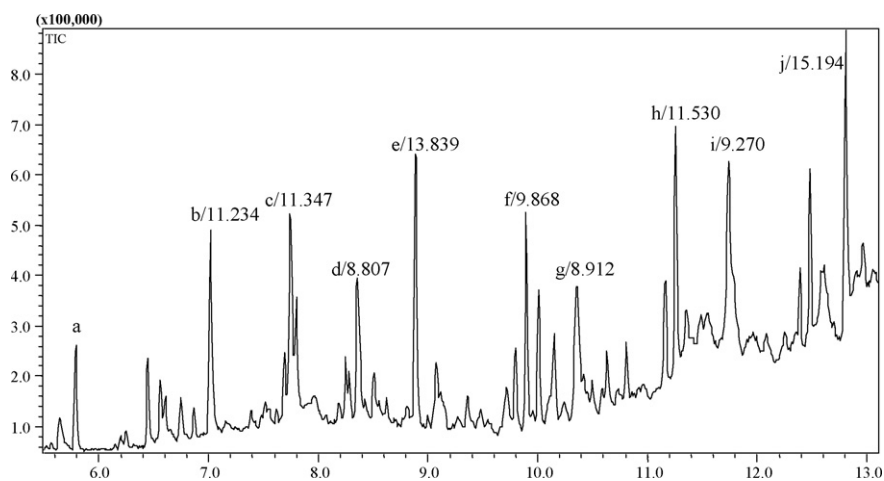
Compounds	Structure	Selectivity (%)
a		19.76
b+c	C <sub>23</sub> H <sub>46</sub> + C <sub>36</sub> H <sub>74</sub>	80.24

compounds were found. In the ozone atmosphere, S element can be directly converted into a kind of gas directly, that is, the total efficiency of desulfurization from thiophene with ozone near to 100%, and the most efficiency desulfurization, assisted by ozone, has been obtained, the reaction conditions was more milder than that of traditional ODS method [11].

#### 4. Catalytic mechanism

Theoretically, the role of ozone on thiophene is a complex oxidation reaction involving double bonds. In the given mechanism, the catalyst behaves as a typical Lewis acid in the oxidation reaction [33].

In this, it forms an anion radical through an electron acceptor, which can add an ozone molecule as shown in Scheme 1. Firstly, oxygen combined with the superacidic Lewis acid sites generated a complex species. It is believed to be the initiation step in the formation of a very reactive primary ozonide intermediate formed by cycloaddition of ozone with thiophene ring in position 2,5, which is followed by rapid thiophene ring cleavage and recombination of the primary ozonide into 2-ene-1,4-dione group [31]. FT-IR spectra due to stretching vibration of keto-carbonyl (about 1680 cm<sup>-1</sup>) conjugated with C=C (about 1600 cm<sup>-1</sup>). Unfortunately a strong band assigned to bending mode of chemisorbed water [29,30] appears in the same region. In this context, it can be assumed that the increas-

**Fig. 10.** GC of the product catalyzed by SZA system (SZA-1.5 h).**Table 4**  
Product distribution of SZA system (SZA-1.5 h)

Compounds	Structure	Selectivity (%)
a+b+c		22.58
d+e		22.65
f–j	Hydrocarbon	54.77

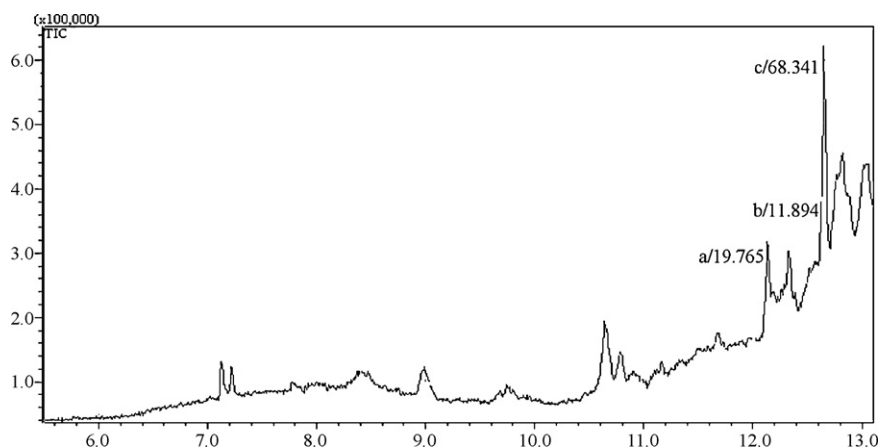
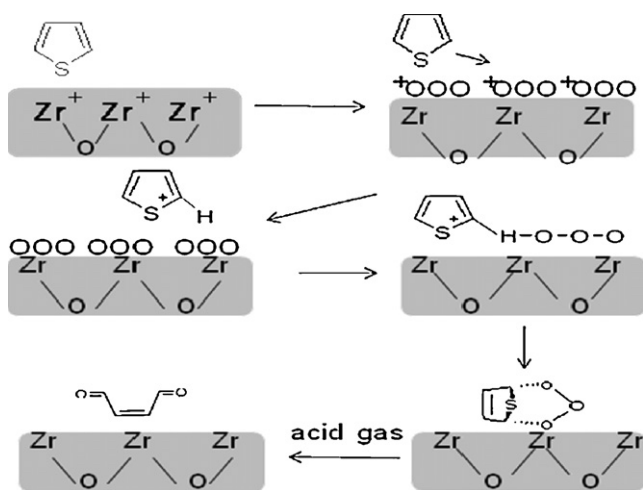


Fig. 11. GC of the product catalyzed by SZO system (SZO-0.5 h).



Scheme 1. Possible mechanism for the main reactions of thiophene with  $\text{SO}_4^{2-}/\text{ZrO}_2$  as the catalyst.

ing of absorbance in the region of  $1700\text{--}1600\text{ cm}^{-1}$  observed after ozonization is due to stretching vibration bands of ketonic double bonds  $\text{C}=\text{O}$  near  $\text{C}=\text{C}$ , overlapping with the bands of chemisorbed water. The formation of  $\text{C}=\text{O}$  and  $\text{C}=\text{C}$  was also tested by XPS analysis.

## 5. Conclusion

Total efficiency of desulfurization from thiophene with ozone near to 100% has been obtained with the  $\text{SO}_4^{2-}/\text{ZrO}_2$  catalytic oxidation reaction. The efficiency of desulfurization with ozone is higher than that of air, which would meet the demand of sulfur content in gasoline and the regulation for environmental protection.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2008.08.003.

## References

- [1] F.F. Li, L.J. Song, L.H. Duan, X.Q. Li, Z.L. Sun, A frequency response study of thiophene adsorption in zeolite catalysts, *Appl. Surf. Sci.* 253 (2007) 8802–8809.
- [2] A.C. Stern, R.W. Boubel, D.B. Turner, D.L. Fox, *Fundamentals of Air Pollution*, 2nd ed., Academic Press, New York, 1984.
- [3] Y. Okamoto, S. Ishihara, M. Kawano, M. Satoh, T. Kubota, Preparation of Co–Mo/ $\text{Al}_2\text{O}_3$  model sulfide catalysts for hydrodesulfurization and their application to the study of the effects of catalyst preparation, *J. Catal.* 217 (2003) 12–22.
- [4] X.L. Ma, K. Sakanishi, I. Mochida, Hydrodesulfurization reactivities of various sulfur compounds in diesel fuel, *Ind. Eng. Chem. Res.* 33 (1994) 218–222.
- [5] Y. Kanda, T. Aizawa, T. Kobayashi, Y. Uemichi, S. Namba, M. Sugioka, Preparation of highly active ALSBA-15-supported platinum catalyst for thiophene hydrodesulfurization, *Appl. Catal. B* 77 (2007) 117–124.
- [6] R.T. Yang, *Adsorbents: Fundamentals and Applications*, Wiley, New York, 2003, Chapter 10.
- [7] A.J. Hernández-Maldonado, R.T. Yang, Desulfurization of liquid fuels by adsorption via  $\pi$ -complexation with Cu(1)–Y and Ag–Y zeolites, *Ind. Eng. Chem. Res.* 42 (2003) 123–129.
- [8] A. Takahashi, F.H. Yang, R.T. Yang, New sorbents for desulfurization by  $\pi$ -complexation: thiophene/benzene adsorption, *Ind. Eng. Chem. Res.* 41 (2002) 2487–2496.
- [9] C.P. Huang, B.H. Chen, J. Zhang, Z.C. Liu, Y.X. Li, Desulfurization of gasoline by extraction with new ionic liquids, *Energ. Fuel* 18 (2004) 1862–1864.
- [10] A. Kumagai, H. Fukumoto, T. Yamamoto, Chemical and electrochemical oxidation of thiophene–pyridine thiophene–pyrimidine Co-Oligomers in solutions, *J. Phys. Chem. B* 111 (2007) 8020–8026.
- [11] C. Song, An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel, *Catal. Today* 86 (2003) 211–263.
- [12] D.H. Zhao, F.X. Sun, E.P. Zhou, Y. Liu, A review of desulfurization of light oil based on selective oxidation, *Chem. J. Internet* 6 (2004) 17.
- [13] J. Nehlsen, J. Benziger, I. Kevrekidis, Oxidation of aliphatic and aromatic sulfides using sulfuric acid, *Ind. Eng. Chem. Res.* 45 (2006) 518–524.
- [14] R.J. Gillespie, T.E. Peel, The hammett acidity function for some superacid systems. II. The systems  $\text{H}_2\text{SO}_4\text{--HSO}_3\text{F}$ ,  $\text{KSO}_3\text{F--HSO}_3\text{F}$ ,  $\text{HSO}_3\text{F--SO}_3$ ,  $\text{HSO}_3\text{F--AsF}_5$ ,  $\text{HSO}_3\text{F--SbF}_5$ , and  $\text{HSO}_3\text{F--SbF}_5\text{--SO}_3$ , *J. Am. Chem. Soc.* 95 (1973) 5173–5178.
- [15] B.M. Reddy, P.M. Srekanth, V.R. Reddy, Modified zirconia solid acid catalysts for organic synthesis and transformations, *J. Mol. Catal.* 225 (2005) 71–78.
- [16] X. Cui, H.Z. Ma, B. Wang, H.W. Chen, Direct oxidation of *n*-heptane to ester over modified sulfated  $\text{SnO}_2$  catalysts under mild conditions, *J. Hazard. Mater.* 147 (2007) 800–805.
- [17] S. Wang, S. Matsumura, K. Toshima, Sulfated zirconia ( $\text{SO}_4/\text{ZrO}_2$ ) as a reusable solid acid catalyst for the Mannich-type reaction between ketene silylacetals and Aldimines, *Tetrahedron Lett.* 48 (2007) 6449–6452.
- [18] O.V. Salomatina, T.G. Kuznetsova, D.V. Korchagina, E.A. Paukshtis, E.M. Moroz, K.P. Volcho, V.A. Barkhash, N.F. Salakhutdinov, Effects of the properties of  $\text{SO}_4/\text{ZrO}_2$  solid catalysts on the products of transformation and reaction mechanism of R-(+)-limonene diepoxides, *J. Mol. Catal. A: Chem.* 269 (2007) 72–80.
- [19] M.L. Satuf, R.J. Brandi, A.E. Cassano, O.M. Alfano, Scaling-up of slurry reactors for the photocatalytic degradation of 4-chlorophenol, *Catal. Today* 129 (2007) 110–117.
- [20] H.Z. Ma, J. Li, B. Wang, Esterification and polymerization by catalytic oxidation of cyclohexane at room temperature over modified sulfated  $\text{TiO}_2$  in the air, *Energ. Fuel* 21 (2007) 1859–1862.
- [21] S.H. Teo, H.C. Zeng, Surface and textural properties of network-modified silica as a function of transition metal dopant Zirconium, *J. Phys. Chem. B* 105 (2001) 9093–9100.
- [22] J.A. Navío, G. Colón, M. Macías, J.M. Campelo, A.A. Romero, J.M. Marinas, Catalytic properties of  $\text{ZrO}_2\text{--SiO}_2$ : effects of sulfation in the cyclohexene isomerization reaction, *J. Catal.* 161 (1996) 605–613.
- [23] T. Ishida, N. Choi, High-resolution X-ray photoelectron spectra of organosulfur monolayers on Au(111): S(2p) spectral dependence on molecular species, *Langmuir* 15 (1999) 6799–6806.



- [24] C.D. Wagner, J.A. Taylor, Generation of XPS auger lines by bremsstrahlung, *J. Electron Spectrosc. Relat. Phenom.* 20 (1980) 83–93.
- [25] Z. Paal, X.L. Xu, J. Paal-Lukacs, W. Vogel, M. Muhler, R. Schlogl, Pt-Black catalysts sintered at different temperatures: surface analysis and activity in reactions of *n*-hexane, *J. Catal.* 152 (1995) 252–263.
- [26] J.R. Sohn, S.H. Lee, J.S. Lim, New solid superacid catalyst prepared by doping ZrO<sub>2</sub> with Ce and modifying with sulfate and its catalytic activity for acid catalysis, *Catal. Today* 116 (2006) 143–150.
- [27] C. Morterra, G. Meligrana, G. Cerrato, V. Solinas, E. Rombi, M.F. Sini, 2,6-Dimethylpyridine adsorption on Zirconia and sulfated Zirconia systems. An FT-IR and microcalorimetric study, *Langmuir* 19 (2003) 5344–5356.
- [28] V. Bolis, G. Magnacca, G. Cerrato, C. Morterra, Microcalorimetric characterization of structural and chemical heterogeneity of superacid SO<sub>4</sub>/ZrO<sub>2</sub> systems, *Langmuir* 13 (1997) 888–894.
- [29] B. Li, R.D. Gonzalez, An in situ DRIFTS study of the deactivation and regeneration of sulfated zirconia, *Catal. Today* 46 (1998) 55–67.
- [30] C. Morterra, G. Cerrato, Brosted acidity of a superacid sulfate-doped ZrO<sub>2</sub> system, *J. Phys. Chem.* 98 (1994) 12373–12381.
- [31] W. Czerwinski, J. Nowaczyk, K. Kania, Ozonization of electronic conducting polymers. I. Copolymers based on poly [3-nonylthiophene], *Polym. Degrad. Stabil.* 80 (2003) 93–101.
- [32] H.Z. Ma, F.T. Chen, B. Wang, Modified SO<sub>4</sub><sup>2-</sup>/Fe<sub>2</sub>O<sub>3</sub> solid superacid catalysts for electrochemical reaction of toluene with methanol, *J. Hazard. Mater.* 145 (2007) 453–458.
- [33] A. Corma, H. Garcia, Naphthalene included within all-silica zeolites: influence of the host on the naphthalene photophysics, *Chem. Rev.* 102 (2002) 3837–3849.