

出國報告（出國類別：參加國際研討會）

參加第五屆化學、化工與化學製程國際 研討會(CCECP 2017)

服務機關：國立嘉義大學

姓名職稱：李茂田 教授

派赴國家：新加坡

出國期間：2017年3月5日至8日

報告日期：2017年4月13日

摘要

CCECP已邁入第五屆，地點都在舉辦在新加坡，CCECP是一個小型但專精在化學化工領域的研討會，參與者來自各國的大學教授與研究學生，非常適合學生去進行口頭報告與學習，透過研討會的交流，可以很直接且詳細地了解到其他國家的化學化工研究。因為主題為化學化工領域，主題明確，與會人員可以很親近的與他人進行對話交流。此次訓練學生在國際研討會以英語口頭發表，也是第一次用英文與外籍朋友溝通整天。對本校的學生，經由此種國際研討會的經驗，提升其程度與視野，是對學生及重要的培養工作。

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目的

至新加坡參加第五屆化學、化工與化學製程國際研討會(CCECP 2017)，進行口頭發表”On the oxidative desulfurization of fuels”研究。

過程

本次參加的會議是由 Global Science and Technology Forum 所舉辦的第三屆化學、化工與化學製程國際研討會(CCECP 2017)，地點位於新加坡，會議時間為 2017 年 3 月 6 號至 7 號。CCECP 與其他幾項研討會一同舉辦在新加坡的 M Hotel，一開始由 GSTF 主席 Stephen Martin 進行開幕致詞，後續每個會議的參與人員再分別到各別的會議室進行會議，CCECP 安排在 ANSON 1 房間。本次會議邀請 2 位學者分別進行一小時的主題演講，首先由來自澳洲 School of Chemistry, The University of Melbourne 的 Spas D Kolev 教授分享他的研究成果”Hybrid flow systems integrating online leaching and online separation for automatic dynamic fractionation and speciation of inorganic arsenic and organic and inorganic mercury in environmental solids”，本會議第二位演講者 Department of Chemistry, National University of Singapore 的 Suresh Valiyaveetil 助理教授，結束後開始進行其他論文發表。本會議共有 9 篇論文發表，參與人員來自台灣、中國、印度、斯里蘭卡、日本、韓國與土耳其的老師與學生，我們的論文被安排在 12:35-12:55，進行 20 分鐘的英文口頭報告與問題討論。後續 1:15-2:15 進行餐會，下午繼續進行論文發表會議，大約在 4 點時結束所有口頭發表會，開始進行由 Kolve 教授主持的 Panel Session，並由幾位老師在板書上進行討論，最後再頒發本次研討會的 Best Paper Awards 與 Best Student Paper，並以大合照結束本次會議。

心得與建議事項

CCECP 已邁入第五屆，地點都在舉辦在新加坡，CCECP 是一個小型但專精在化學化工領域的研討會，參與者來自各國的大學教授與研究學生，非常適合學生去進行口頭報告與學習，透過研討會的交流，可以很直接且詳細地了解到其他國家的化學化工研究。因為主題為化學化工領域，主題明確，與會人員可以很親近的與他人進行對話交流。在會場內時，與 CCECP 的主席 Kolve 教授有熱烈的直接對話。餐敘時間主動與斯里蘭卡的 Arasaretnam Selladurai 老師認識。由於彼此都是有相同的學術背景，本系博班學生沈子堯與來自中國廈門大學博士班 楊昭同學與日本名古屋大學的女碩士生 地多玲子同學三人，密切交談，在中午餐敘時間一同享受午餐與交流，互相留下聯絡方式。

沈子堯同學第一次在國際研討會以英語口頭發表，也是第一次用英文與外籍朋友溝通整天。對本校的學生，經由此種國際研討會的經驗，提升其程度與視野，是對學生及重要的培養工作。研討會過後，學生也了解到自己不足之處，需要再加強改進，對一個博士班學生而言，參加 CCECP 是個非常難得且寶貴的經驗，使其受益良多。

會議流程

CCECP 2017 Tentative Conference Program

DAY 1

Date: 6 March 2017 (Monday)

Venue: M hotel, Singapore

Room: Anson III

9:00-9:30	Registration
9:30-9:45	Opening Address Venue: Anson III Prof. the Hon. Dr. Stephen Martin Chairman, Board of Governors, Global Science & Technology Forum (GSTF) Chief Executive, Committee for Economic Development of Australia (CEDA) Chairman, Bank of China (Australia) Former Speaker Parliament of Australia Former Deputy Vice Chancellor (Strategy and Planning) Curtin University of Technology Former Pro Vice Chancellor International, Victoria University
9:45-10:05	Coffee / Refreshment Break Please head to your conference room (Maxwell)
10:05-10:50	Keynote Address: <i>"Hybrid flow systems integrating Online Leaching and Online Separation for Automatic Dynamic Fractionation and Speciation of Inorganic Arsenic and Organic and Inorganic Mercury in Environmental Solids"</i> Prof. Spas D Kolev School of Chemistry The University of Melbourne Victoria, Australia
10:50-11:35	Keynote Address: <i>"Design, Synthesis and Characterization of Functionalized Nanosilica"</i> Assoc. Prof. Suresh Valiyaveetil Department of Chemistry National University of Singapore
11:35-11:55	CCECP 17 "Highly Selective Hydrogenation of Pyrrole on Ru/C Catalyst: Effect of the Pretreatment and Ru Particle Size" Prof. Zhao Yang and Mr. Bing H Chen Xiamen University, China
11:55-12:15	CCECP 6 "Molar Heat Capacity of Aqueous Solutions of Tertiary Amine 1-Dimethylamino-2-propanol with Polyamine Diethylenetriamine" Prof. Meng-Hui Li Chung Yuan Christian University, Taiwan

12:15-12:35	CCECP 11 "Modification and Cation Adsorption Studies of Polyphenols Extracted from Acacia Farnesiana" Dr. Arasaretnam Selladurai Eastern University, Sri Lanka
12:35-12:55	CCECP 23 "On the Oxidative Desulfurization of Fuels" Prof. Maw-Tien Lee National Chia-Yi University, Taiwan
12:55-1:15	CCECP 5 "Thermal storage property of Metal PCM core / Al₂O₃ Shell Structure Ball for High Temperature Range" Ms. Reiko Chida Nagoya University, Japan
1:15-2:15	LUNCH
2:15-2:35	CCECP 26 "First Immobilized Catalysts for Iridium-Catalyzed Asymmetric Allylic Amination – Rate Enhancement by Immobilization" Ms. Richa Gupta and Dr. Chandi Malakar National Institute of Technology Manipur, India
2:35-2:55	CCECP 15 "Process configuration and economic analysis of Direct DME (dimethyl ether) process from FOG" Ms. Jeongeun Son Inha university, South Korea
2:55-3:15	CCECP 27 " Effect of the Dopant Atom on the Electronic and Structural Properties of C₂₀ Fullerenes" Prof. Mustafa Şenyel Anadolu University, Turkey
3:15-3:35	CCECP 20 "Studies on Reaction Kinetics for Synthesis of Cardanol-Furfural Resin" Dr. Ashwani Kumar Rathore H. B. Technical University, Kanpur, India
3:35-4:20	Panel Session by Dr. Spas Kolev
4:20-4:40	BEST PAPER AWARD & BEST STUDENT PAPER AWARD
4:40-5:00	Coffee / Refreshment Break

與會照片



筆者於會場

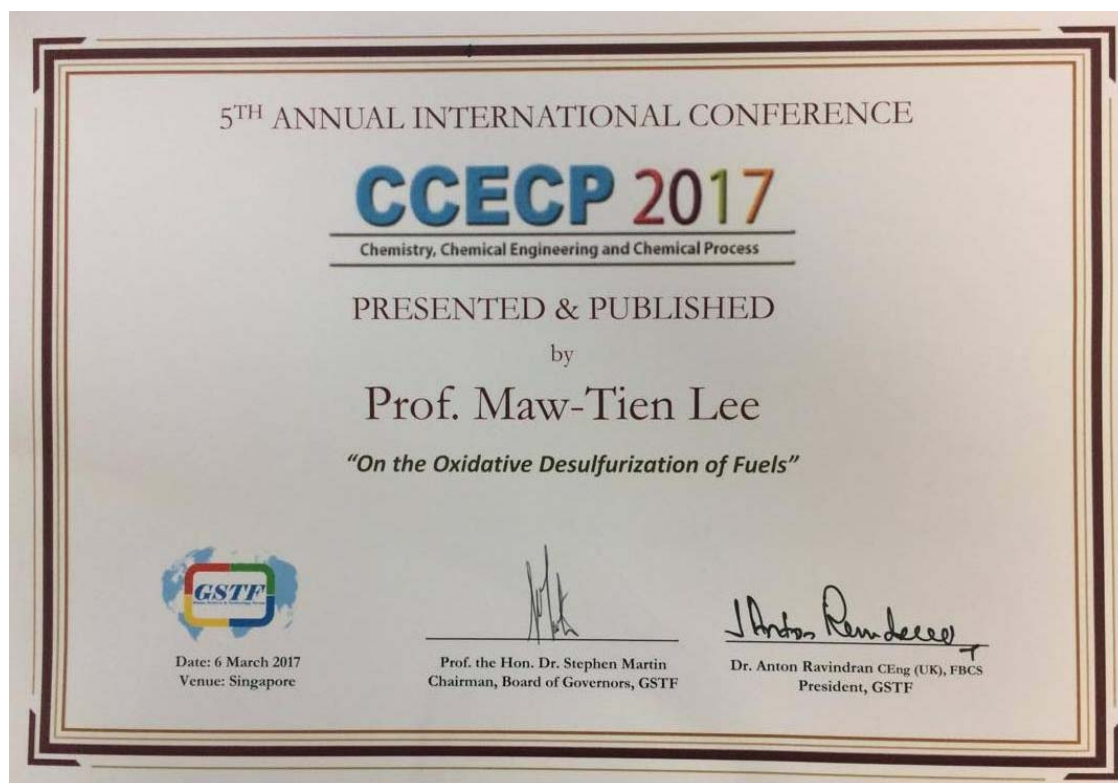


筆者於會場



筆者與澳洲墨爾本大學 Kolve 教授合照
本次研討會(CCECP)的主席

大會頒發的口頭發表證書





On the Oxidative Desulfurization of Fuels

Zih-Yao Shen

6 March 2017

Zih-Yao Shen^a, Hwei-Ping Shih^a, Tzong-Bin Lin^b, Maw-Tien Lee^c

^aDepartment of Applied Chemistry, National Chia-Yi University, Chia-Yi City, Taiwan

^bRefining and Manufacturing Research Institute, CPC Corporation, Chia-Yi City, Taiwan

Outline



Introduction

Experiments

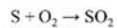
Results and discussion

Conclusions

Introduction - why is sulfur removed from oil



Sulfur content in crude oil ranges from 0.03% - 7.89%



- SO₂ is a colorless gas which is dangerous to human health
- SO₂ emissions are a precursor to atmospheric particulates
- SO₂ causes acid rain (H₂SO₄)

Nationwide Diesel Sulfur Limits (parts per million)

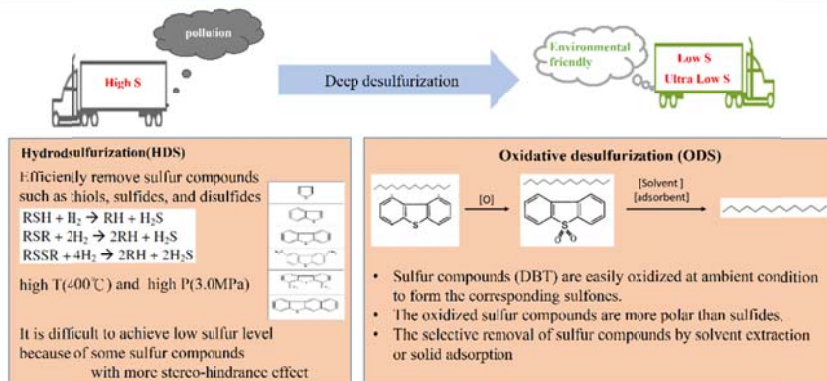
Country	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020
Brazil*	500	2500								500						
China*	5000								500		50					
EU-27	50			10												
India*	500					350										
Japan	50		10													
Russia	300								350		50	10				
Thailand	150															
USA	500	15														
South Africa	5000	150	50	50	50	50	50	50	50	50	50	50	50	50	50	50

Gasoline Sulfur Limits (parts per million)

Country	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020
Brazil*	300									50						
China*	500					150										
EU-27	50			10												
India*	500					150										
Japan	50		10													
Russia	300								150		50	10				
Thailand	150															
USA	500/500/500	50 (avg) / 50 (avg)														
South Africa	5000	150														

Source: transportpolicy.net, trace elemental instruments.net, EN 590:2009, US EPA

Introduction - how to remove sulfur from oil



Introduction - pyrolysis gasoline



Typical composition of Pyrolysis Gasoline

PyGas Components	Weight percent (wt %)
Benzene, toluene and xylenes	50
Olefins and dienes	25
Styrene and other aromatics	15
Paraffins and naphthenics	10

A by-product of naphtha cracking during ethylene and propylene production

A highly unsaturated hydrocarbon mixture (C5s to C12s)

PyGas can be blended with other hydrocarbons as a gasoline additive or the source of BTX

PyGas contains undesirable heteroatom containing hydrocarbons such as organic sulfur compounds

Sulfur level are typically in the 100 to 1000 ppm

The material often cannot be used because of the high sulfur concentration

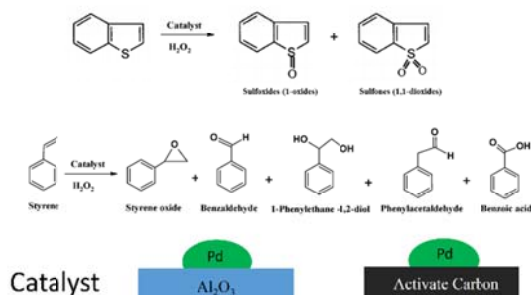
De Vries, J. L., et al. (2017) A review on the 'next stage' of naphtha cracking, *Reaction Journal of Chemical Engineering*, 242, 119-131

Al, David (2012) The hydrogenation of pyrolysis gasoline (PyGas) over nickel and palladium catalysts, PhD thesis, University of Glasgow.

Experiments

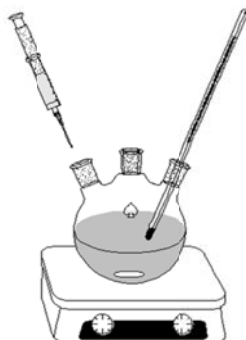


The oxidation reaction of **benzothiophenes** and **styrene** to their corresponding oxidation product.



Journal of Catalysis 198, 179–186 (2001)
Catal. Sci. Technol., 5, 325–338 (2015)

Experiments



①

20g Model compounds in the reactor
500 ppm benzothiophene and 500ppm styrene in n-Octane

②

Solution was heated to 69°C, 75°C or 85°C

③

Catalyst and oxidant were injected into a batch reactor

20g H_2O_2 with 0.1g $\text{Pd}/\text{Al}_2\text{O}_3$ / 20g H_2O_2 with 0.1g Pd/AC

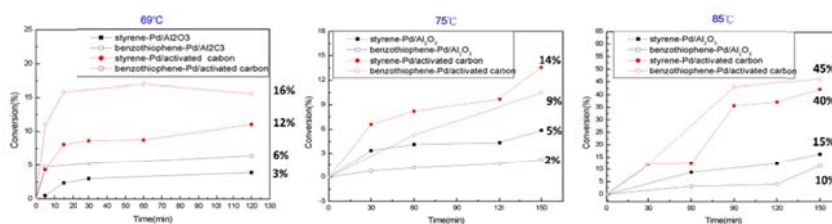
④

The mixtures were sampled **every ten minutes** to analyze the conversion of benzothiophene and styrene with a gas chromatography

Results



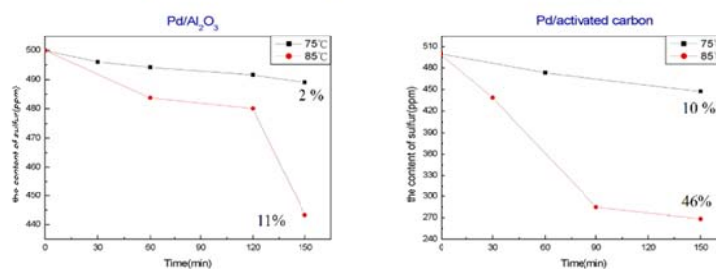
The conversion of benzothiophene and styrene by $\text{Pd}/\text{Al}_2\text{O}_3$ and Pd/AC catalysts at different temperature



Results



Effect of reaction temperatures and times on oxidative desulfurization by $\text{Pd}/\text{Al}_2\text{O}_3$ and Pd/AC catalyst



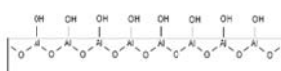
From the two graphs, Pd/AC catalyst have better desulfurization performance in this system

Results



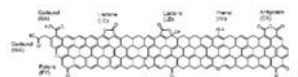
The conversion of benzothiophene and styrene at 69°C, 75°C and 85°C by Pd/Al₂O₃ and Pd/AC catalyst

Temperature	69°C		75°C		85°C	
Pd/support	Al ₂ O ₃	AC	Al ₂ O ₃	AC	Al ₂ O ₃	AC
Benzothiophene conversion(B)	6%	16%	1.5%	10%	10%	45%
Styrene conversion (S)	3%	12%	5%	12%	15%	40%
Selectivity (B/S)	2	1.33	0.33	0.83	0.67	1.12



surface structure of the aluminum oxide

surface area of aluminum oxide: 120 m²/g



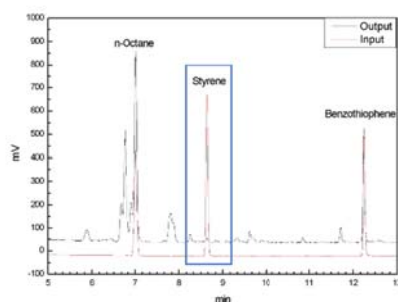
surface groups on activated carbon

surface area of the activated carbon: 1050 m²/g

Optical Engineering, 2011, 50 (7), pp 071109-071109.

J. Chem. Educ., 2015, 92 (1), pp 143-147

Results



GC-FID chromatograms of model compound before and after oxidation by Pd/activated carbon at 150°C

Conclusions



1. The oxidation reaction with Pd/AC catalyst had greater conversion than that of reaction with Pd/ Al₂O₃ catalyst.
2. It is better for the removal of sulfur compounds in Pd/AC catalyst system at certain temperature.

On the Oxidative Desulfurization of Fuels

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1. Abstract

In this paper, we used an oxidative desulfurization method to oxidize model compounds (500 ppm benzothiophene and 500 ppm styrene) to simulate the desulfurization of fuels. The conversion and the selectivity of benzothiophene and styrene were observed. The catalyst was prepared by loading Pd atom on supports, Aluminium oxide (Al_2O_3) and Activated Carbon (AC) respectively. Hydrogen peroxide (35%) was used as oxidant with Pd/ Al_2O_3 or Pd/AC as catalysts. Reactions occurred at 69°C, 75°C and 85°C respectively. Experimental results showed that the reaction with catalyst Pd/AC had greater conversion for both benzothiophene and styrene than that of the reaction with Pd/ Al_2O_3 as catalyst. However the Pd/AC catalyst had greater desulfurization efficiency for removing benzothiophene than that of the reaction with Pd/ Al_2O_3 catalyst.

Keywords: oxidative desulfurization, benzothiophene

2. Introduction

The sulfur in transportation fuels may convert to toxic SO_x , which contributes to the air pollution and the acid rain. Deep desulfurization of diesel fuels has become an important research subject due to the upcoming legislative regulations to reduce sulfur content in the world. US Environmental Protection Agency has set up guidelines to limit the sulfur content of diesel fuels to 15 ppm by 2006. The environmental regulation for on-road diesel fuels planned in Europe call for a sulfur content to 50 ppm by 2005 and to 10 ppm by 2009. Similarly, in Japan the sulfur concentration will be below 50 ppm by the end of 2004. In Taiwan, the regulation for the sulfur content in diesel fuels will be lower

than 50 ppm by 2005.

Hydrodesulphurization (HDS) is the conventional process to remove thiols, sulfides, and disulfides in the petroleum industry. However, it is difficult to achieve an ultralow sulfur level because of some refractory sulfur compounds such as dibenzothiophene (DBT) and its derivatives. Owing to their stereo-hindrance, severe operating condition and large capital cost are required for HDS to achieve ultralow desulfurization of fuels. [1] Therefore, alternative desulfurization technologies are desired. Oxidation [2,3,4,5,6,7,8,9], extraction [10,11,12,13,14], adsorption [15,16,17,18] and bioprocesses[19,20] have received wide attention recently.

During the oxidative desulfurization, sulfur compounds can be oxidized by the electrophilic addition of oxygen atoms to the sulfur to form sulfoxides (1-oxides) and sulfones (1,1-dioxides). The chemical and physical properties of sulfoxides and sulfones are significantly different from those of hydrocarbons in fuels, and consequently they can be more easily removed by distillation, solvent extraction, adsorption or decomposition.

Most fuels are refined products of the petroleum industry and contain aliphatic, olefins, alkenes and aromatics etc. The common aromatic compounds within fuels include toluene, benzene, xylene, styrene, BT, DBT, etc. [21,22,23] The literatures have showed a lot of adsorbents with an excellent efficiency for removing sulfur compounds, but few studies focused on reducing the loss of olefin or paraffin hydrocarbon compounds during desulfurization process. In order to understand the loss of olefins in fuels during desulfurization process, styrene was chosen as the olefin model compound and BT was chosen as the sulfur model compound in this study. Experimental results showed that the reaction with Pd/AC had greater conversion for both benzothiophene and styrene than that of the reaction with Pd/Al₂O₃ as catalyst. However the Pd/AC catalyst had greater desulfurization efficiency for removing benzothiophene and less styrene loss than that of the reaction with Pd/ Al₂O₃ catalyst.

3. Materials and Methods

The ingredients of commercial fuels are too complicated, therefore we conducted the experiment with model compounds which have benzothiophene, styrene in n-hexane or n-octane. First, solutions with 500 ppm benzothiophene and 500ppm styrene were

dissolved in n-hexane (69°C) or n-octane (75°C and 85°C). Catalysts, Pd/Al₂O₃ and Pd/AC, were prepared by impregnating method. Model compounds were heated to 69°C, 75°C or 85°C and hydrogen peroxide with Pd/Al₂O₃ or Pd/AC was injected into a batch reactor containing model compounds. The mixtures were sampled every ten minutes to analyze the conversion of benzothiophene and styrene. A gas chromatography (Shimadzu GC-14A) with DB-5 column and FID was used to analyze the samples. The GC temperature was programmed to keep 5 minutes at 40°C and then heated to 200°C at a rate of 20°C per minute. It was kept at 200°C for 2 minutes. The carrier gas (N₂) flow rate was 25mL per minute. The injection temperature of GC was 225°C and the detector temperature was 250°C in our experiments.

4. Results and Discussion

Scheme 1 gives the possible mechanism of the reaction system. Under the experimental conditions as mentioned above, the sulfides and aromatic sulfur compounds can be oxidized by hydrogen peroxide to the corresponding sulfoxides (1-oxides) and sulfones (1,1-dioxides).

Figure 2 shows that the maximum conversion of benzothiophene and styrene is about 6% and 3% respectively with Pd/Al₂O₃ catalysis at 69 °C. The conversion of benzothiophene is twice as that of styrene.

Figure 3 shows that the maximum conversion of benzothiophene and styrene is about 2% and 5% respectively with Pd/Al₂O₃ catalyst at 75°C. The selectivity of oxidation of benzothiophene is about half that of styrene. Figure 3 shows that the maximum conversion of benzothiophene and styrene is about 9% and 14% respectively with Pd/AC catalyst at 75°C.

Figure 4 shows that the maximum conversion of benzothiophene and styrene is about 9% and 15% respectively with Pd/Al₂O₃ catalyst at 75°C. The selectivity of oxidation of benzothiophene is about half that of styrene. Figure 4 also shows that the maximum conversion of benzothiophene and styrene is about 45% and 40% respectively with Pd/AC catalyst at 75°C.

Table 1 gives the comparison of Pd/Al₂O₃ and Pd/AC at various temperatures. The oxidation reaction at 85°C had greater conversion than that of the reaction at the lower temperature and the conversion of benzothiophene and styrene with Pd/AC catalyst at 85

°C is much more than the others.

Fig. 5 and Fig. 6 demonstrate the effect of reaction temperature and reaction time on the oxidative desulfurization efficiency by Pd/AC catalyst. As shown in the figures, the content of sulfur compounds in fuels decreased with the increase of the reaction time and most of sulfur compounds removed completed within 150 min. It is also shown that high temperature (85°C) is better for the removal of sulfur compounds than that of low temperature (75°C). The reaction with Pd/AC catalyst achieved a removal of 46% of sulfur and the reaction with Pd/Al₂O₃ catalyst only removed 11% of sulfur. It is clear that Pd/AC catalyst performed better performance than that of Pd/Al₂O₃ catalyst in this system.

On the basis of above results, activated carbon is better than Al₂O₃ to be a supporter for oxidative desulfurization. The large surface area, porous structure and many surface oxygen-containing functional groups, such as C=O or COOH with activated carbon are the advantage for it to be used as the supporter. In addition, activated carbon is more hydrophobic than Al₂O₃, so it shows a high affinity towards oil phase. The Pd/AC catalyst dispersed in oil phase is more well than that of the Pd/ Al₂O₃ catalyst, which lead to the higher oxidation performance.

Conclusion

1. The oxidation reaction with Pd/AC catalyst had greater conversion than that of reaction with Pd/ Al₂O₃ catalyst.
2. High temperature is better for the removal of sulfur compounds for Pd/AC catalyst system.

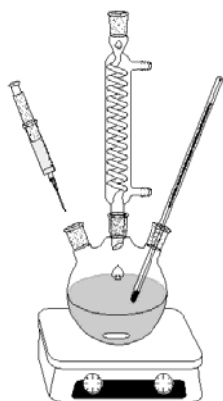
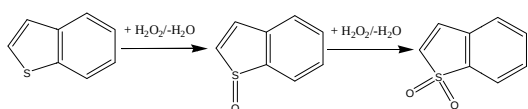


Figure 1: experimental apparatus



Scheme 1 [24]

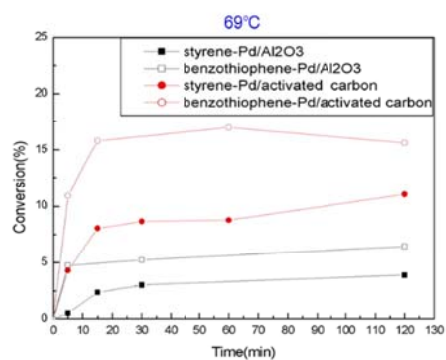
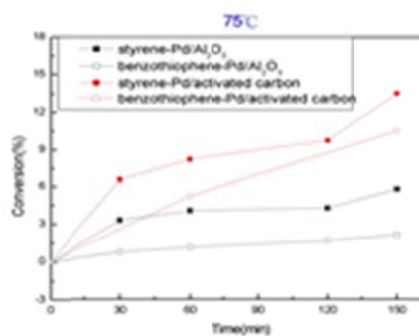


Figure 2: the conversion of benzothiophene and styrene at 69°C by Pd/Al₂O₃ and Pd/AC catalyst.

Figure 3: the conversion of benzothiophene and styrene at 75°C by Pd/Al₂O₃ and Pd/AC catalyst.



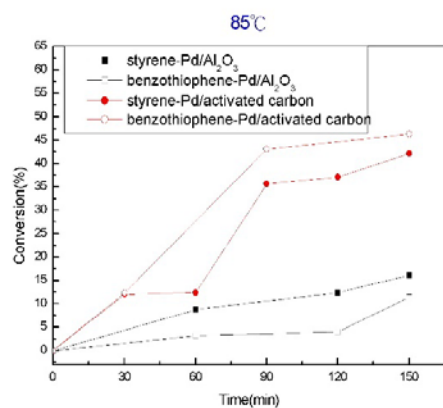


Figure 4: the conversion of benzothiophene and styrene at 85°C by Pd/Al₂O₃ and Pd/AC catalyst.

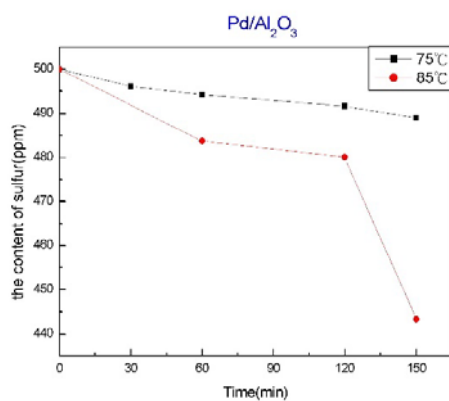


Figure 5: effect of reaction temperature and time on oxidative desulfurization by Pd/Al₂O₃ catalyst.

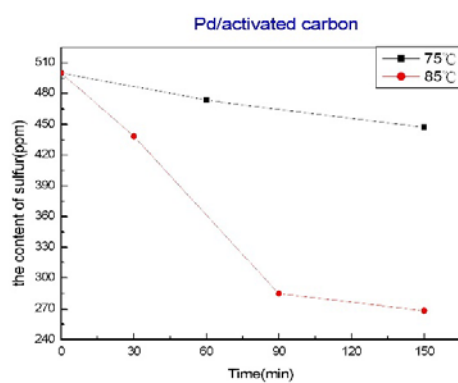


Figure 6: effect of reaction temperature and time on oxidative desulfurization by Pd/AC catalyst.

Table 1: The conversion of benzothiophene and styrene at 69°C, 75°C and 85°C by Pd/Al₂O₃ and Pd/AC catalyst.

Temperature	69°C		75°C		85°C	
Catalyst	Pd/Al ₂ O ₃	Pd/AC	Pd/Al ₂ O ₃	Pd/AC	Pd/Al ₂ O ₃	Pd/AC
Benzothiophene conversion(B)	6%	16%	1.50%	9%	10%	45%
Styrene conversion (S)	3%	12%	4.50%	12%	15%	40%
Selectivity (B/S)	2	1.33	0.33	0.75	0.67	1.12

5. References

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