Petroleum & Coal
ISSN 1337-7027

Available online at www.vurup.sk/petroleum-coal
Petroleum & Coal 57(3) 291-294, 2015

OXIDATION OF DIBENZOTHIOPHENE USING OXYGEN AND A COPPER PHOSPHOTUNGSTATE CATALYST FOR DEEP DESULFURIZATION OF FUELS

Jianwei Ding, Rui Wang*

*School of Environmental Science and Engineering, Shandong University, No. 27 Shanda South Road, Jinan 250199, P.R.China.*Email: ree_wong@hotmail.com*

Received April 8, 2015; Accepted June 11, 2015

Abstract

A Keggin structure copper phosphotungstate catalyst shows considerable catalytic activity in the oxidation of dibenzothiophene(DBT) using molecular oxygen and air as oxidant under mild reaction conditions. The influence of the catalyst dosage and oxidant flow rate on desulfurization was investigated. The oxidation activity performance of air is close to molecular oxygen at same conditions. A remarkable DBT conversion appears when the air flow rate is 800mL/min. Nearly 97% DBT conversion is achieved in 30min. This provides a new pathway to realize green oxidative desulfurization of fuels with oxygen as oxidant.

Key words: desulfurization; oxygen; air; copper phosphotungstate.

---

1. Introduction

Presently, environmental pollution is one of the problematic issues worldwide, the environment common hazardous materials that exist in our environment are NOx, SOx, COx, volatile organic compounds (VOCs), nitrogen-containing compounds (NCCs), sulfur-containing compounds (SCCs)and so on. Sulfur compounds are common impurities in fossil fuel. The reduction in the level of sulfur compounds is very necessary and important because of the air pollution from SOx and the adverse impact on human health [1-2], such as corrosion, air pollution and acid rain which endanger human health [3]. Therefore, to investigate and develop a deep desulfurization technology of high efficiency and great stability has become a worldwide research focus.

Oil desulfurization technology can be simply divided into hydrodesulfurization (HDS) and non-hydrodesulfurization (NHDS). HDS is a conventional process utilized to produce fuels of low sulfur contents, but the investment and operation costs are very high. However, it is difficult to reduce refractory sulf-containing compounds such as dibenzothiophene (DBT) and its derivatives. Oxidative desulfurization (ODS), applied as one kind of NHDS methods, has shown to be one of the most promising procedures because of its great potential to produce ultra clean fuels [4]. ODS is a highly selective and effective approach for removing heterocyclic sulfur compounds, which can have a favorable effect even under mild reaction condition [5-7].

H_2O_2 is the highly reactive oxidant mostly used for ODS [8-10], but the use of H_2O_2 suffers from some shortcomings, such as the low utilization efficiency of H_2O_2 and emulsion-separation with fuels [11-12]. Other oxidants like organic and inorganic peroxyacids, and O_3 have also been reported for ODS [13-15]. Taking into account environmental and economic concerns, the utilization of O_2 as the oxidant for ODS is most desirable [16-17]. Our investigation herein, adopting molecular oxygen and air as the oxidant, used copper phosphotungstate for the first time as a kind of efficient catalytic material and provided a new pathway to realize deep desulfurization of refractory sulfur compounds from model oil under eco-sustainable conditions.

2. Experimental

2.1 Materials

All the reagents used in the preparation of the composite material were used as received. AR-grade phosphotungstic acid ($H_3PW_{12}O_{40}\cdot xH_2O$) and copper nitrate were purchased from the from Tianjin Kermel chemical reagent co., ltd., China; Ethanol absolute (purity ≥ 99.5%) was purchased from Tianjin Fuyu Fine Chemistry Co., Ltd., China; The chemicals used for desulfurization experiments: dibenzothiophene and n-octane were also used as received. Dibenzothiophene ($C_{12}H_8S$, 99%) was purchased from Sigma-Aldrich. A certain amount of dibenzothiophene (DBT, 99%) was dissolved in octane to obtain the model oil.

2.2 Catalyst preparation

The catalyst of $Cu_{1.5}PW_{12}O_{40}\cdot 15H_2O$ was prepared according to literature method with improvement [18]. The phosphotungstic acids was dried under 230°C for 3 h before use. A amount of phosphotungstic acid (HPW,30g) was dissolved in the mixture of distilled water and ethanol with stirring, and copper nitrate ($Cu(NO_3)_2\cdot 3H_2O$, 3.5g) was added in the mixture in sequence, continuous stirring of the mixture was performed for about 1h at room temperature to make it produced double decomposition reaction, the equation was shown as follow: $H_3PW_{12}O_{40}+1.5\ Cu(NO_3)_2 \quad Cu_{1.5}PW_{12}O_{40}+3HNO_3$. After that the mixture was heated at 80°C to remove ethanol and then was slowly cooled to room temperature. The product was obtained by crystallizing and ageing the above mixture to dryness at 120°C for 6 h.

2.3 Experimental method

A certain amount (0.123g) of dibenzothiophene (DBT, 99%) was dissolved in 60 mL octane three flask to obtain the model oil with 500mg/L (500 ppm) sulfur content in it, and then 60 mL distilled water was added as extraction agent. The mixture was stirred at 90 °C for 10 min by water bath approach. The left of the flask connected with a gas tube through which oxygen was introduced into the reaction solution at a constant rate, one of the two side necks connected with a water-cooled reflux condenser to prevent reaction solution loss, and the other was closed with glass stopper. Oxygen was bubbled into the mixed liquid, followed by the addition of catalyst. Reaction liquid in octane phase were sampled respectively at a series of reaction time and then analyzed with microcoulometer.

3. Results and discussion

3.1. Catalytic oxidative desulfurization process (ODS)

3.1.1 Influence of the catalyst dosage

The effect of amount of $Cu_{1.5}PW_{12}O_{40}\cdot 15H_2O$ in the catalytic process was investigated. Increasing the amount of catalyst improved the sulfur removal performance. The results indicated that it is difficult to achieve deep sulfur levels without $Cu_{1.5}PW_{12}O_{40}\cdot 15H_2O$. As can be seen from Figure 1, at the same reaction conditions, the curve for 0.421g (1% the mass of normal octane) catalyst showed a different final percentage of sulfur removal compared to non-catalyst. The efficiency of the catalytic desulfurization was much higher than that of non-catalytic (36% higher). The DBT conversion was increased with the dosage of catalyst. When the dosage was increased to 3% the mass of normal octane, the efficiency of the DBT conversion was 76% at 150 min.

3.1.2 Influence of the oxygen flow rate

In oxidative desulfurization reaction, the effect of oxidant was important. Therefore, the influence of the oxygen flow rate was studied. The results were shown in Figure 2, the rate of reaction increased with oxygen flow rate, and a higher extent of sulfur removal was achieved within 100 mL/min. The efficiencies of oxidative desulfurization decreased in the order of 100 mL/min > 90mL/min > 80 mL/min. However, there is a downward trend when the reaction to 90min with the the oxygen flow rate was 100 mL/min. Under those conditions, solvent volatilization rate increased rapidly, so the DBT conversion decreased by degrees. The curves for 90 mL/min and 80 mL/min had similar trends with the time. At the optimal conditions, the DBT conversion was reached to 78%.

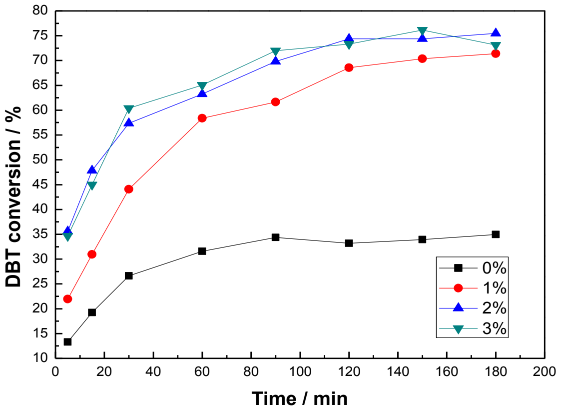

Fig. 1 Oxidative desulfurization effect of different catalyst dosage

Experimental conditions: initial sulfur concentration, 500 ppm; reaction temperature, 90°C; oxidant, O_2; the flow rate of O_2, 90 mL/min; extracting agent, distilled water.

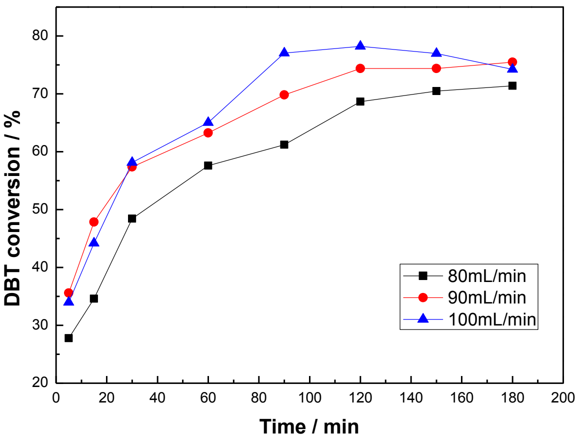

Fig. 2 The effect of the oxidant flow rate on the $Cu_{1.5}PW_{12}O_{40}\cdot 15H_2O$

Experimental conditions: initial sulfur concentration, 500 ppm; reaction temperature, 90°C; oxidant, O_2; catalyst dosage, 2% the mass of normal octane; extracting agent, distilled water.

3.1.3 Controlled experiments with air as oxidant

Air was also utilized as oxidant for desulfurizaton. Comparing the efficiency of desulfurization with others, the oxygen flow rate with 90 mL/min had higher and more stable DBT conversion which was 75% in 180 min. On the basis of these results, 90mL/min was chosen as the suitable condition to compare with air. To ensure the actual oxygen feed rate equivalent to 90 mL/min O_2, the air flow rate was set as 450 mL/min. After 90 min, 74% of the DBT was oxidized and removed from model oil. Then the DBT conversion has a downward trend with the solvent volatilization rate increased. The oxidation activity performance of air was close to molecular oxygen at the same conditions. Increasing the air flow rate from 450mL/min to 800mL/min led to a remarkable enhancement of the conversion of DBT. At the same conditions, the efficiency of the DBT conversion could reach 97% in 30min and the downward trend was not obviously. It is practically feasible to use air as oxidant in desulfurization, which are more economical and greener.

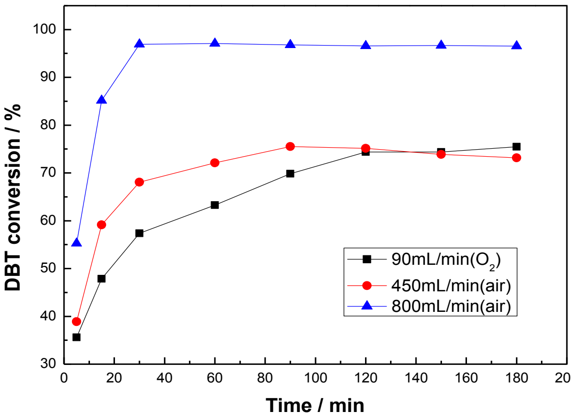

Fig. 3 The effect of the air flow rate on the $Cu_{1.5}PW_{12}O_{40}\cdot 15H_2O$

Experimental conditions: initial sulfur concentration, 500 ppm; reaction temperature, 90°C; oxidant, O_2 or air; catalyst dosage, 2% the mass of normal octane; extracting agent, distilled water.

4. Conclusions

In conclusion, we synthesized the catalyst of copper phosphotungstate which showed considerable catalytic activity in the oxidation of DBT by using oxygen and air. This provides a new pathway for the ODS of fuels with oxygen as oxidant.

Acknowledgments

We acknowledge the financial support from the National Natural Science Foundation of China (Nos. 20976097, 21076116, 21211120165, 21311120297), Petro China Scientific and Technical Innovation Project (2010D-5006-0405), and Natural Science Foundation of Shandong Province (ZR2011BM023).

References

[1] Jiang D, Su L, Ma L, et al., Cu–Zn–Al mixed metal oxides derived from hydroxy-carbonate precursor for H_2S removal at low temperature, Appl. Surf. Sci. 2010; 256: 3216–3223.
[2] Habibi R., Rashidi A M, Daryan J T, et al., Study of the rod-like and spherical nano-ZnO morphology on H_2S removal from natural gas, Appl. Surf. Sci. 2010; 257: 434–439.
[3] Fang W L. Inventory of U. S. Greenhouse Gas Emissions and Sinks,1990-2003. Clean Air Markets Division, 2004.
[4] Jiang X, Li H M, Zhu W S, et al. Deep desulfurization of fuels catalyzed surfactant-type decatungstates using H_2O_2 as oxidant. Fuel 2009; 88: 431-436.
[5] Zhou X R, Li J, Wang X N, et al. Oxidative Desulfurization of Dibenzothiophene Based on Molecular Oxygen and Iron Phthaocyanine. *Fuel Processing Technology* 2009; 90: 317-323.
[6] Wang R, Yu F L, Zhang G F, Zhao H X. Catalysis Today 2010;150: 37-41.
[7] Lv H Y, Zhang Y N, Jiang Z X, Li C. Green Chemistry 2010;12: 1954-1958.
[8] Tong S P, Shi R, Zhang H, Ma C N. Journal of Environmental Sciences 2010; 22:623-1628.
[9] Wang R, Zhang G F, Zhao H X. Catalysis Today 2010; 149: 117-121.
[10] Wang H, Wang R. Collection of Czechoslovak Chemical Communications 2011; 76: 1595-1605.
[11] Zhou X R, Lv S, Wang H, Wang X N, Liu J H. Applied Catalysis A: General 2011; 396: 101-106.
[12] Jiang Z X, Lv H Y, Zhang Y N, Li C. Chinese Journal of Catalysis 2011; 32: 707-715.
[13] Tam P S, Kittrell J R, Eldridge J W. Ind Eng Chem Res 1990; 29: 321.
[14] Yang L W ,Li J, Yuan X D, Shen J, Qi Y T. J Mol Catal A, 2007; 262: 114.
[15] Zhao Y, Wang R. Petroleum & Coal, 2013; 55 (1): 62-67.
[16] Tang N F, Zhang Y N, Lin F, Lv H Y, Jiang Z X, Li C. Chem Commun 2012; 48: 11647.
[17] Lv H Y, Zhang Y N, Jiang Z X, Li C. Green Chem, 2010; 12: 1954.
[18] Wang R, Jiang H. China Tungsten Industry. 2008; 23 (3): 27-30.