Intensified Reaction of Dilute Thiophenes in Nanoreactor

Li Zhou,*,† Shengqiang Wang,† Wei Dai,‡ and Yaping Zhou‡

High Pressure Adsorption Laboratory, School of Chemical Engineering and Technology, and Department of Chemistry, School of Science, Tianjin University, Tianjin 300072, People's Republic of China

Received: November 7, 2007; In Final Form: November 27, 2007

A discovery that catalytic reactivity is intensified on reducing the size of reactor toward several nanometers scale was applied for the separation of dilute species, for example, the thiophenic compounds in transportation fuels, in the present study. A characteristic reaction of the dilute species was selected as the separation mechanism, and a nanoreactor was formed with preloading reactant/catalyst in volumes of mesopore dimension. Probability for the dilute species to contact the nanoreactor radically enlarged due to the integration of such volumes in a porous material. Because all reagents and the reaction product stayed inside the nanoreactor, separation of fuel from sulfuric compounds and the surplus chemicals used in reaction becomes simple. It was experimentally shown that the nanoreaction exhibited first-order kinetics, and all thiophenes and benzothiophenes contained in different types of model fuels were completely removed at moderate conditions.

I. Introduction

Separation of dilute species bears special importance for environment protection since either gaseous or liquid contaminants are dilutely spread over a bulk phase. Concentration of these contaminants is too low to allow for a separation mechanism to function efficiently and makes the separation a tough job. One of the difficult separations is removing thiophenes from transportation fuels. The catalyst employed for the emission control of vehicles will be poisoned if fuel contains sulfur even at a parts per million level, and serious pollution will then result in emission. Therefore, advances in auto technology are not enough to guarantee clean vehicles. The sulfur level of transportation fuels must match the level of auto technology. However, the desulfurization technologies presently available are not quite efficient enough for the separation of thiophenes from fuels;[1−4] therefore, this group of sulfuric compounds dictates the degree of deep desulfurization, and their removal has attracted a lot of research interests so far.

Excessive chemicals and energy are required if the separation proceeds in bulk phases as is the case of hydrodesulfurization (HDS). The HDS technology saturates the double bond of thiophenes by hydrogenation at temperatures of 300−350 °C and hydrogen pressures up to 2−10 MPa. However, the double bonds of olefins and aromatic hydrocarbons contained in fuels are more reactive than that of thiophenes in the hydrogenation reaction. Therefore, thiophenes cannot be thoroughly removed considering the decrease in fuel quality and increase in cost.[5] Adsorption on activated carbon[6] is not efficient due to lack of selectivity for thiophenes. The mechanism of π-complexion enlarged the adsorption capacity remarkably;[7] however, this mechanism is not thiophene-selective either. The desulfurization function is considerably affected by the existence of aromatic components and the water dissolved in fuel.[8] Similarly, the aromatic components of fuels may invalidate the oxidation/extraction method.[9] Therefore, separation of thiophenic compounds from transportation fuels still appeals for solution.

It is very important for the separation of dilute species that the separation is based on a selective separation mechanism, i.e., the mechanism functions only for the species to be separated. The reaction of thiophenes with formaldehyde catalyzed by a strong acid[10] is such a mechanism, which guarantees the selectivity and reliability of the desulfurization function. However, the mechanism itself is not enough to guarantee a satisfactory desulfurization performance if the reaction occurs in bulk phases. Tremendous chemicals must be consumed, and the separation of fuel from the surplus reagents and the reaction product constitutes another tough job. The present study shows a selective reaction that occurring in reactors of nanometer dimension may provide dilute species an efficient separation.

Studies in nanoscience revealed that reduction in reactor size down to several nanometers scale might cause a favorite change in catalytic activity.[11] Advantage is shown presently when the required catalyst/reactant are preloaded in a volume of nanometer dimension forming a nanoreactor. Probability of the dilute species to contact the reactor enlarged radically than in bulk media due to the collection/integration of such volumes. Because all reagents and the reaction product stayed inside the nanoreactor, purification of fuel becomes an easy job for liquid/solid-phase separation. Natural or artificial porous material with pore dimension of several nanometers may be qualified to make the nanoreactor. The present work aims to show the advantage and feature of the nanoreactor for the separation of dilute species in term of removing dilute thiophenes from transportation fuels.

2. Experimental Section

2.1. Preparation of Nanoreactor. The condensation reaction of thiophenes with formaldehyde catalyzed by a strong acid is taken for the mechanism of separating thiophenes from fuel since other components of fuel are inert at specified reaction conditions. By consideration of the load of reagents and

---

* To whom correspondence should be addressed. Phone and Fax: +86 22 8789 1466. E-mail: zhouli@tju.edu.cn.

† School of Chemical Engineering and Technology, Tianjin University.

‡ School of Science, Tianjin University.

10.1021/jp710660t CCC: $40.75

diffusion resistance, the nanoreactor is better at mesopore dimensions, and SBA-15 and CMK-3, the synthesized silica and carbon mesoporous material with orderly structure,[12,13] were initially used to make the nanoreactor. However, their high manufacturing cost prohibits them from practical application; therefore, mesoporous silica gels and mesopore-rich activated carbons were also tested as nanoreaction carriers. Sulfuric acid, hydrochloric acid, and heteropolyacids were consecutively used as the catalyst of the reaction. Catalysts were preloaded in the nanoreactor by titration (for sulfuric acid), vapor adsorption (for hydrochloric acid), or soaking in solution (for heteropolyacids). The loading method of formaldehyde is associated with the nanoreaction carrier and the method of loading catalyst. For example, formalin liquid was dropped in silica gel if the vapor of hydrochloric acid (HCl) had been previously adsorbed. However, formaldehyde (vapor of formalin) was carrying on by a stream of nitrogen and passed a packing bed of activated carbon and adsorbed in the carbon, on which sulfuric acid had been previously dropped in.

2.2. Preparation of Model Fuels. Desulfurization performance of the nanoreactor was tested in model fuels. Hundreds of sulfuric compounds may appear in liquid fuels; therefore, model fuels are usually used for the research of deep desulfurization.[14] The key component in deep desulfurization is thiophenes; therefore, thiophene was used as the representative sulfuric compound to prepare model fuels. Since the reactivity of aromatic and aliphatic hydrocarbons may be different for the reaction, three types of model fuels were prepared. Octane was used as the representative aliphatic fuel (ALF), and benzene was used as the representative aromatic fuel (ARF), and a mixture composed of 80% octane and 20% benzene was used as representative mixed type fuel (MXF). The content of thiophene in all model fuels is 2000 ppm (equivalent to 760 ppm of elemental sulfur). A gas chromatograph model GC 4000A was used to analyze the concentration of thiophene in fuels.

2.3. Performance Tests. The desulfurization performance was examined first in batch tests and then in continuous flows through a packing bed. The former aimed to allocate an appropriate reaction condition, and the latter aimed to evaluate the capacity of a nanoreactor at the appropriate condition. The reaction temperature was maintained constant at a specified value by circulating water through a thermostat. Breakthrough curves were collected on continuous tests, from which the sulfur capacity was calculated

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

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

Where Q_b is sulfur breakthrough capacity per unit mass of adsorbent in wt%,

Q_s is sulfur saturation capacity per unit mass of adsorbent in wt %,

υ is flow rate of model fuel in cm^3 min^{-1},

ρ is density of model fuel at normal temperature and pressure, g cm^{-3},

c_i is initial sulfur content in ppm,

m is mass of adsorbent in packing bed in g,

c_t is sulfur content at time in ppm,

x_i is sulfur content in wt %,

t_b is the time sulfur breaks through the packing bed in min, and

t_s is the time for $c_t/c_i = 1$ in min.

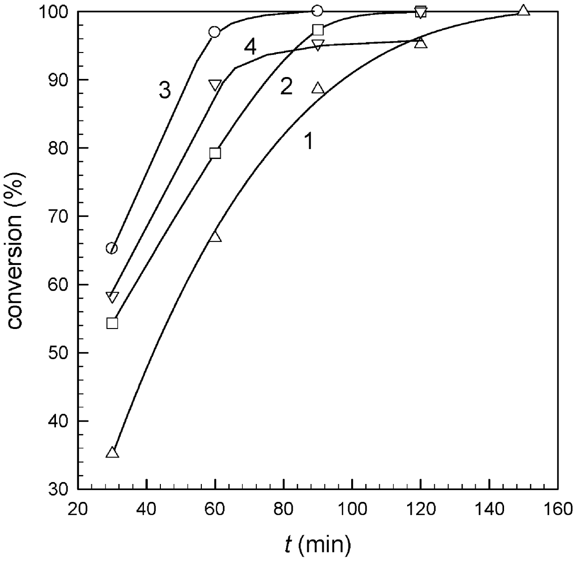

Figure 1. Conversion rate of thiophene at different temperatures. 1, 50 °C; 2, 60 °C; 3, 70 °C; 4, 80 °C (AC-BY1 loading formaldehyde and sulfuric acid in ARF fuel).

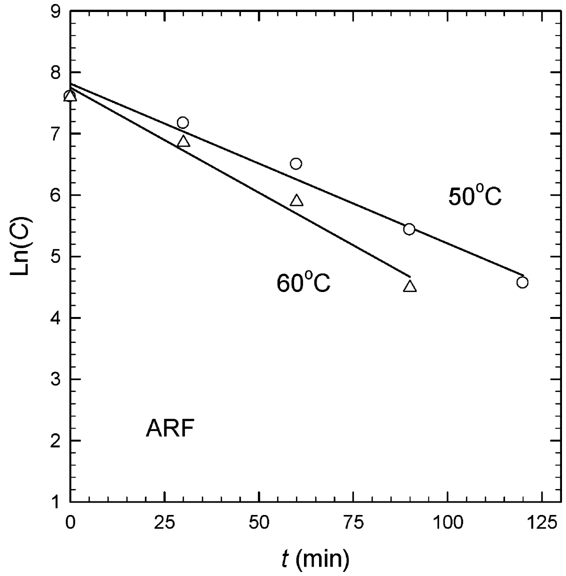

Figure 2. Plots for the determination of reaction order (AC-BY1 loading formaldehyde and sulfuric acid in ARF fuel).

3. Results and Discussion

3.1. The Quasi-First-Order Dynamics of Nanoreaction. Because catalyst and all reactants, except for the one spreading in fuel, were preloaded in the nanoreactor, their concentrations must be higher than the thiophene that came across the nanoreactor. Therefore, the rate of nanoreaction must be quasi-first order as a rule.[15] A typical experimental result of batch tests is shown in Figure 1, from which plots for the determination of reaction order can be drawn and shown in Figure 2. Thiophene converted to sulfuric resin in the nanoreactor, and the resin was there adsorbed. Therefore, the percentage conversion of Figure 1 is the percentage removal of element sulfur from fuel. Letter c of Figure 2 is the concentration of thiophene in fuel at time t. Linearity is shown on plots, which means the reaction order is first. Of course the reaction is not of genuine

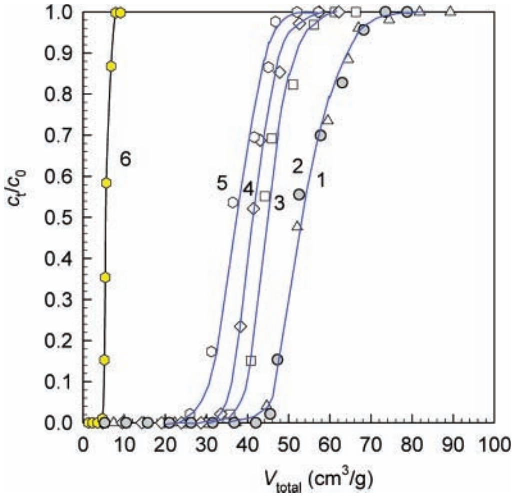

Figure 3. Breakthrough curves of thiophene in MXF fuel. 1 and 2, packed with nanoreactor made of CMK-3 or AC-BY1; 3, packed with nanoreactor made of AC-NM3; 4, packed with nanoreactor made of AC-JX104; 5, packed with nanoreactor made of AC-KW1; 6, packed with only AC-BY1. 70 °C.

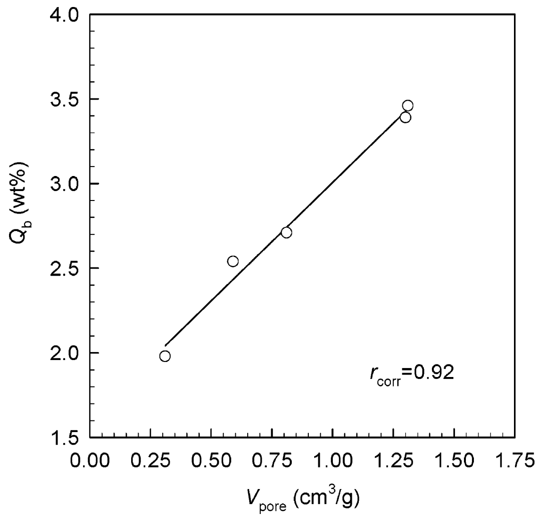

Figure 4. Correlation of breakthrough capacity (in MXF fuel) of nanoreactor with its pore volume.

TABLE 1: Pore Dimension of Carbon Materials Tested

carbon	S_{BET}/m^2 g^{-1}	V_{pore}/cm^3 g^{-1}	d_{norm}/nm	Q_b/wt %
AC-BY1	2207	1.31	2	3.46
CMK-3	1098	1.30	3.8	3.39
AC-NM3	1515	0.81	1.5	2.71
AC-JX104	1048	0.59	1.2	2.54
AC-KW1	347	0.31	1	1.98

first-order kinetics due to the two reactants (thiophene and formaldehyde) and a catalyst joining the reaction. However, the excessive quantity of formaldehyde and catalyst in a nanoreactor renders the reaction rate depending only on the concentration of thiophene and showing the quasi-first-order dynamics.

3.2. Effect of Temperature. The rate of nanoreaction is faster at higher temperatures as shown in Figure 1. The time needed to completely remove the 2000 ppm thiophene from fuel becomes shorter and shorter as temperature increases from 50 to 70 °C. However, the conversion rate dropped down at 80 °C due possibly to the too much loss of formaldehyde. Therefore, 70 °C is appropriate for the characteristic nanoreaction.

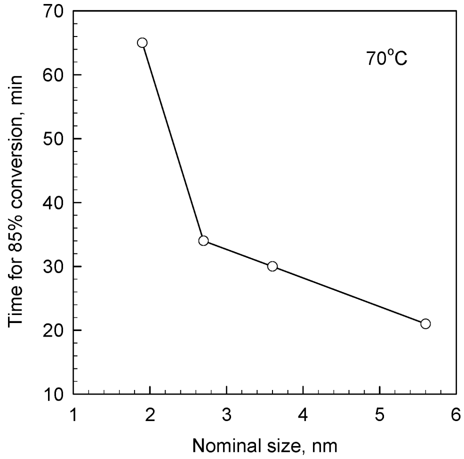

Figure 5. Variation of conversion time with nanoreactor dimension.

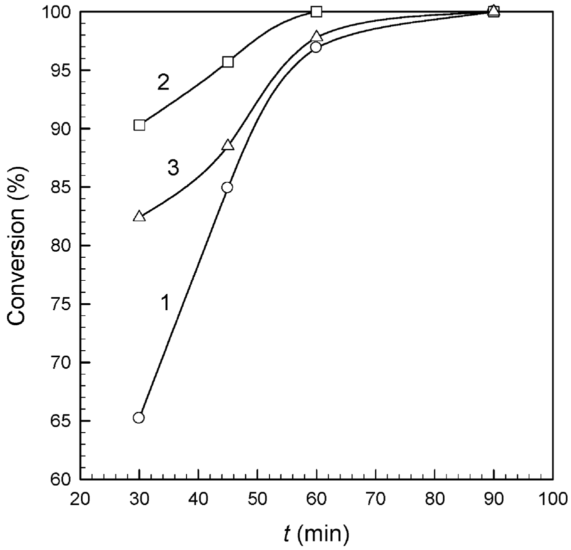

Figure 6. Compatibility of desulfur function with fuel types. 1, ARF; 2, ALF; 3, MXF.

3.3. Effect of Nanoreactor Dimension. To observe the effect of nanoreactor dimension, the experimental results with nanoreactors made of different porous carbon materials are shown in Figure 3. The major pore dimension data of these materials are given in Table 1. The longer the break time, the larger the sulfur capacity. Curve 6 belongs to activated carbon AC-BY1 without loading reagents. The break time is quite short; therefore, the sulfur capacity of the carbon is little if the desulfurization mechanism is adsorption only. However, the sulfur capacity becomes nearly ten times larger if a nanoreactor is made of the carbon as shown by curve 1. Curve 1 almost represents the performance of nanoreactors made of mesomolecular sieve CMK-3 and activated carbon AC-BY1. As shown in Table 1, the specific surface area of these is two times different; however, their pore volume is almost same. Correlation of the breakthrough capacity of nanoreactors with their pore volume is shown in Figure 4. The correlation is linear with a correlation coefficient of 0.92. Therefore, pore volume exerts the major effect on the sulfur capacity of nanoreactor. The nominal size of nanoreactor also exerts important effect on the desulfurization performance. The larger the nanoreactor dimension, the less the diffusion resistance, and the faster the rate of reaction as shown in Figure 5. The ordinate of the figure is the time for 85% conversion of thiophene, and the abscissa is the nominal size of nanoreactors. The other condition of the nanoreaction is same. It is, therefore, concluded, a nanoreactor with nominal size of larger than ca. 2.5 nm and larger volume will show the best performance of desulfurization.

3.4. Other Features of the Proposed Method. Desulfurization tests were carried out in different types of model fuels, and the 2000 ppm thiophene was completely removed in all cases as shown in Figure 6. Although the reaction rate is faster in aliphatic than in aromatic fuel, there is not much difference. The dissolved water may retard the reaction rate a little but not to invalidate the desulfurization function at all. The selective separation mechanism functions also for benzothiophenes. By replacement of thiophene with 4,6-dimethyldibenzothiophene (4,6-DMDBT) to prepare model fuels, complete removal of the sulfuric compound was also observed in all types of model fuels with/without the presence of dissolved water, though the required time is a little longer than for thiophene.

4. Conclusion

1. Nanoreactor is reliable and efficient for the separation of dilute species as proven by the example of removing thiophenes from the different types of model fuels.

2. Nanoreaction exhibited quasi-first-order reaction dynamics due to the excessive quantity of catalyst/reactants (except the one to be separated) in the nanoreactor.

3. The condensation reaction of thiophenes with formaldehyde is a selective separation mechanism. Either the double bonds in other hydrocarbons or the dissolved water does not invalidate the desulfurization function.

4. Separation performance could be optimized with tuning the reaction temperature and the dimension of nanoreactors. Larger than ca. 2.5 nm of nominal size and larger specific volume is preferred in making a nanoreactor.

Acknowledgment. Support of the National Natural Science Foundation of China (#20336020 and #20776099) is sincerely acknowledged.

References and Notes

(1) Knudsen, K. G.; Cooper, B. H.; Topsøe, H. *Appl. Catal. A* **1999**, *189*, 205.

(2) Babich, V.; Moulijn, J. A. *Fuel* **2003**, *82*, 607.

(3) Bej, S. K.; Maity, S. K.; Turaga, U. T. *Energy Fuels* **2004**, *18*, 1227.

(4) Song, C. *Catal. Today* **2003**, *86*, 211.

(5) Whitehurst, D. D.; Isoda, T.; Mochida, I. *Adv. Catal.* **1998**, *42*, 345.

(6) Zhou, A. N.; Ma, X. L.; Song, C. S. *J. Phys. Chem. B* **2006**, *110*, 4699.

(7) Yang, R. T.; Hernandez-Maldonado, A. J.; Yang, F. H. *Science* **2003**, *301*, 79.

(8) Kim, J. N.; Ko, C. H.; Park, J. G.; Han, S. S.; Cho, S. H.; Bhandarl, V. M. *AIChE Annual Meeting*, **2005**, #385b, Cincinnati, Ohio, U.S.A.

(9) Chica, A.; Corma, A.; Domine, M. E. *J. Catal.* **2006**, *242*, 299.

(10) Caesar, P. D.; Sachanen, A. N. *Ind. Eng. Chem.* **1948**, *40*, 922.

(11) Graeser, M.; Pippel, E.; Greiner, A.; Greiner, A.; Wendorff, J. H. *Macromolecules* **2007**, *40*, 6032.

(12) Zhou, L.; Liu, X. W.; Sun, Y.; Li, J. W.; Zhou, Y. P. *J. Phys. Chem. B* **2005**, *109*, 22710.

(13) Liu, X. W.; Zhou, L.; Li, J. W. Sun, Y.; Su, W.; Zhou, Y. P. *Carbon* **2006**, *44*, 1386.

(14) Hernandez-Maldonado, A. J.; Yang, R. T. *Ind. Eng. Chem. Res.* **2003**, *42*, 3103.

(15) Wang, Z. L.; Zhou, Y. P.; Li, S. L. Liu, J. J. *Physical Chemistry, Part II*, 4th ed.; Senior Education Press: Beijing, 2001; pp 203−206.