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Kinetics and mechanism of liquid-phase oxidation of thiophene over TS-1 using H_2O_2 under mild conditions

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Thiophene is a typical thiophenic sulfur compound in gasoline. Using *n*-octane containing thiophene as the model compound, the oxidation of thiophene, which is a key step for the oxidative deep desulfurization of gasoline, was carried out to study the reactivity of thiophene in oxidation reactions. It has been observed that thiophene oxidation can occur using water or *t*-butanol as solvent. Kinetics of the reaction shows a pseudo-first-order toward thiophene or catalyst and a zero order toward hydrogen peroxide. The mechanism for this unique reaction was proposed as the activation of conjugated electron in thiophene ring.

KEY WORDS: thiophene; oxidation; titanium silicalite; hydrogen peroxide; desulfurization.

1. Introduction

The removal of organosulfur compounds present in petroleum has received increasing attention in recent years primarily for environmental reasons. The desulfurization technique commonly used is catalytic hydrodesulfurization, which fails or becomes uneconomical to meet a more stringent sulfur level of liquid fuels. Many refiners favor oxidative desulfurization (ODS) under mild conditions as an alternative or complementary technology to HDS for deep desulfurization. This process preferentially treats benzothiophene, dibenzothiophene and their corresponding alkyl derivatives with hydrogen peroxide over various catalysts such as acetic acid [1–7], formic acid [8–10], polyoxometalate [10–13] and Ti-containing molecular sieves [14,15]. However, the application of the ODS process does not work as well on desulfurization of gasoline, owing to the large amount of thiophene (Th) and alkyl-substituted thiophenes in it [16]. Traditionally, it is believed that thiophene-including alkyl derivatives are highly stable heterocyclic compounds and cannot be oxidized by hydrogen peroxide under mild conditions [8]. In this paper, we report a very efficient way to remove thiophene by oxidation process over TS-1. Various kinetic parameters of this reaction are examined and the reaction mechanism of thiophene is proposed.

2. Experimental

2.1. Materials

Thiophene, analytical grade from China, was used without further treatment. Hydrogen peroxide (aqueous solution 30%, China) was used as oxidant. Its concentration was determined by iodometric titration and its consumption was not monitored during the reaction.

Methanol, analytical grade (China), acetonitrile, analytical grade (China), *t*-butanol, analytical grade (China) and ion-free water were used as solvent, respectively.

2.2. Catalysts

Titanium silicalite TS-1 prepared using tetra-propyl ammonium bromide (TPABr) as the template, according to reference [17], was used as the catalyst.

2.3. A typical reaction run

In a typical run, the water bath was first heated up and stabilized to the desired reaction temperature (293 K–353 K). Then, 0.01 mL thiophene was dissolved in 10 mL *n*-octane and added to the water-bathed jacket flask. 0.05–0.10 g of the catalyst and 10 mL solvent containing H_2O_2 at H_2O_2/sulfur mol ratio 1.2 : 1–4 : 1 were added to the reactor. The resulting mixture was stirred for 6 h at the reaction temperature and analyzed periodically. Catalysts were centrifuged off and the organic phase was subjected to gas chromatographic analysis with an FID detector on a capillary column (SE-54, 15m × 0.25mm, 0.33μm film thickness). Oxida-

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tion products were identified through GC-MS analysis and Ion Chromatograph analysis (Biotronic, Germany, IC-1000).

2.4. Conversions and reaction rates

The conversion of thiophene was calculated using its initial concentration (C_0) and concentration after t min (C_t). Thiophene conversion x is expressed as

$$x = \frac{C_0 - C_t}{C_0}$$

assuming that the volume and mass of the reaction mixtures were constant, since only small amounts of liquid samples were withdrawn during the reaction.

If thiophene oxidation follows pseudo-first-order reaction kinetics toward substrate thiophene, then the apparent rate constant k and reaction time t can be described using the following equation:

$$\ln\left(\frac{C_t}{C-0}\right) = -kt$$

where

$$k = A\mathrm{e}^{-E_a/RT}$$

A is the preexponential factor, E_a is the apparent activation energy; R and T are the gas constant and the reaction temperature (K) respectively.

3. Results and discussion

3.1. Oxidation of thiophene in different solvents

We compare the results of oxidation of thiophene in different solvents (figure 1). It has been shown that the removal of thiophene from model gasoline (composed of n-octane containing thiophene) by oxidation in different solvents increased in the following order: water > t-butanol > methanol ≈ acetonitrile. However, not all these thiophene removal were due to the oxidation reaction. When methanol or acetonitrile is used as solvent, only the increasing adsorption of thiophene to the TS-1 catalyst contributes to the removal of thiophene from the n-octane phase in 6 h, and this has been confirmed by experiment without H_2O_2 (figure 2). While in solvent water, thiophene conversion dramatically increased in 6 h, compared to the blank test without H_2O_2. In this case, thiophene had been completely oxidized to sulfuric acid, which was traced out in the water phase and was further identified by depositing $BaSO_4$. The other oxidation products of thiophene except sulfuric acid have been analyzed by GC-MS. And, in water phase, there were mainly oxidation products such as the corresponding butanedioic acid and propanedioic acid in the presence of excessive hydrogen peroxide; large amount of styrene was detected in oil phase, and trace amount of styrene was also detected in water phase. The oxidation reaction also proceeds in t-butanol but at a relatively low reaction rate compared to that in solvent water. The conversion of thiophene remains constant after 6 h at H_2O_2/thiophene ratio 1.2 : 1 because of the total consumption of oxidants. As indicated in table 1, when more H_2O_2 is added, the final conversion of thiophene increases until no more thiophene can be detected by FID.

3.2. Kinetics of oxidation of thiophene

Reaction kinetics is of great importance in explaining the reaction mechanism. Experiments to obtain kinetics parameters of the oxidation of thiophene were carried

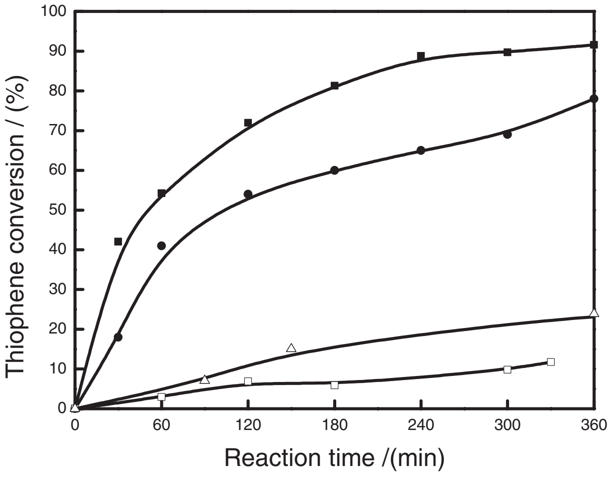


Figure 1. Oxidation of thiophene in various solvents. (■) water, (●) t-butanol, (△) methanol, (□) acetonitrile. Reaction condition: TS-1 $10 \mathrm{gL}^{-1}$, 333 K, 1 atm, H_2O_2 : Thiophene = 1.2 : 1.

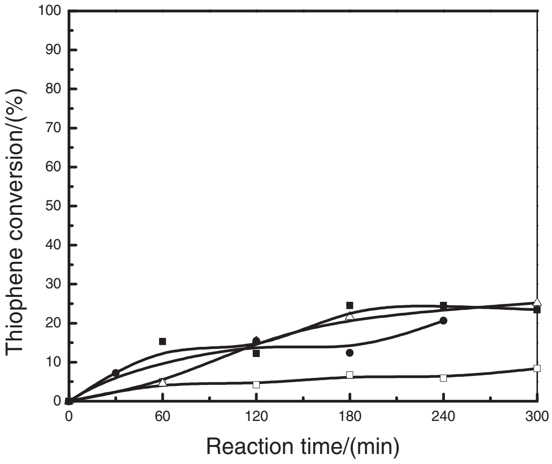


Figure 2. Contribution of thiophene adsorption onto catalyst on the total thiophene conversion (■) water, (●) t-butanol, (△) methanol, (□) acetonitrile. Reaction condition: TS-1 $10 \mathrm{gL}^{-1}$, 333 K, 1 atm, without addition of H_2O_2.

Table 1
Degree of thiophene removal for various H_2O_2/Thiophene ratio[a]

H_2O_2/Thiophene ratio (mol: mol)	x (%)
1.2	91.59
2.0	95.28
3.0	96.88
4.0	98.28

[a]Reaction condition: 333 K, 6 h, water as solvent.

out in TS-1/water/n-octane system, and the reaction rate may be expressed as

$$v = k[cat.]^{\alpha}[Th]^{\beta}[H_2O_2]^{\gamma}$$

In this novel triphase system for thiophene oxidation, a consistent linear reaction kinetics for thiophene over TS-1 (constant during the reaction) in excessive amount of H_2O_2 was demonstrated in the plot of $\ln C_t/C_0)$, as a function of reaction time (figure 3). The oxidation reaction follows the pseudo-first-order toward substrate thiophene under the settled condition, complied with the postulation in Section 2.4. Then the reaction order of catalyst was determined by changing the concentration of the catalyst in the above reaction system. The apparent rate constants for other amount of catalyst were also obtained by following the disappearance of thiophene in n-octane (figure 4). Obviously, thiophene was oxidized much faster over larger amount of TS-1 (table 2). A linear logarithm plot for apparent reaction rate constant against catalyst concentration (figure 5) shows that the reaction order for the catalyst was

$$\alpha = 1.325 \approx 1$$

Pseudo-zero-order toward hydrogen peroxide was also determined following the same method (figure 6).

The effect of reaction temperature on the thiophene oxidation using hydrogen peroxide over TS-1 catalyst is shown in figure 7, where the conversion of thiophene versus time is plotted. It can be seen that temperature influences the catalytic oxidation of thiophene. Reaction rate increases when temperature rises from 293 to 353 K. A linear Arrhenius plot of the first-order reaction rate constants is also obtained by analyzing the graph of the reaction temperature (figure 8), and the apparent activation energy E_a was 29.86 kJ mol^{-1} under the condition.

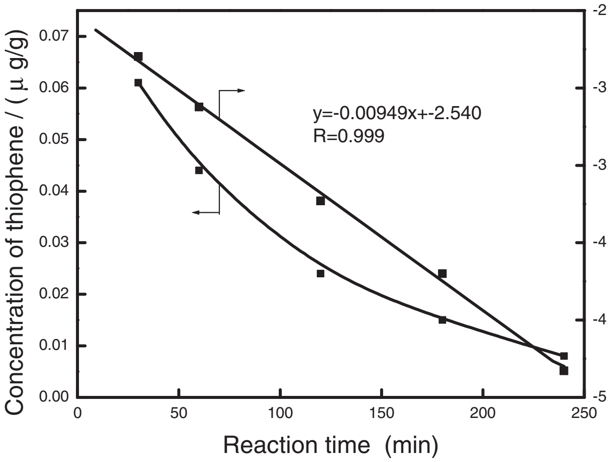


Figure 3. Changing of thiophene concentration during the reaction and $\ln(C_t/C_0)$ as a function of reaction time. Reaction condition: TS-1 10gL^{-1}, 333 K, 1 atm.

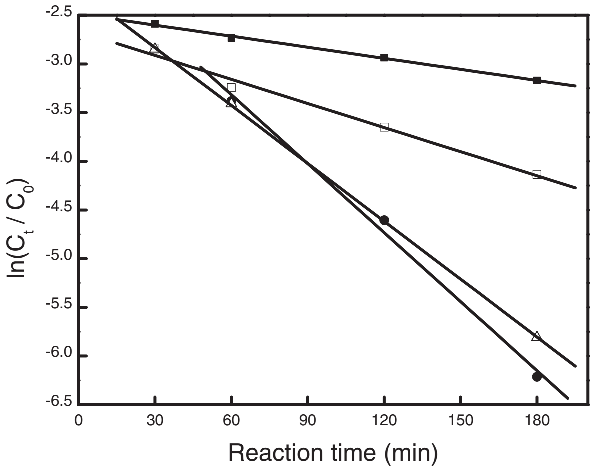


Figure 4. Pseudo-first-order rate constants for different TS-1 catalyst concentration at 333 K. (■) 5gL^{-1}, (□) 10gL^{-1}, (△) 15gL^{-1}, (●) 20gL^{-1}.

3.3. Mechanism aspects of oxidation of thiophene

When water is used as the solvent, the reaction is generally considered as being performed in a triphase system (Solid– liquid–liquid), which has significantly enhanced the activity and para-selectivity of aromatic compounds over the TS-1 catalyst [18–21]. It was reported that this was due to the Brönsted acidity of

Table 2
The apparent rate constants of thiophene oxidation for various amount of catalyst[a]

Catalyst concentration	Apparent rate constant k	Correlation factor R
(gL^{-1})	(min^{-1})	
5	0.00379	0.999
10	0.00809	0.997
15	0.01684	0.989
20	0.02274	0.997

[a]Reaction condition: 333 K, H_2O_2/Thiophene (mol) = 4 : 1

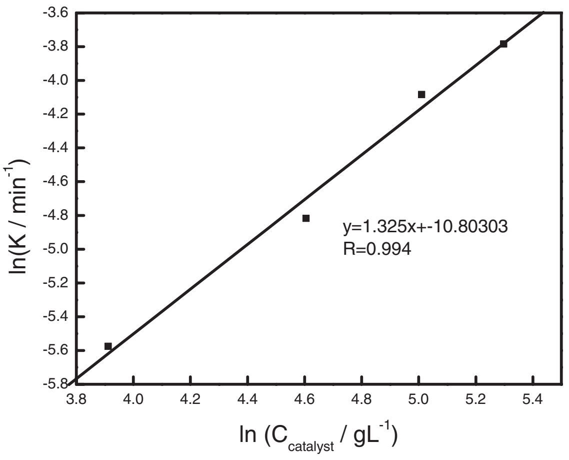


Figure 5. Pseudo-first-order rate constants for catalyst in the oxidation of thiophene. Reaction condition: TS-1 10gL^{-1}, 333 K, 1 atm, solvent water.

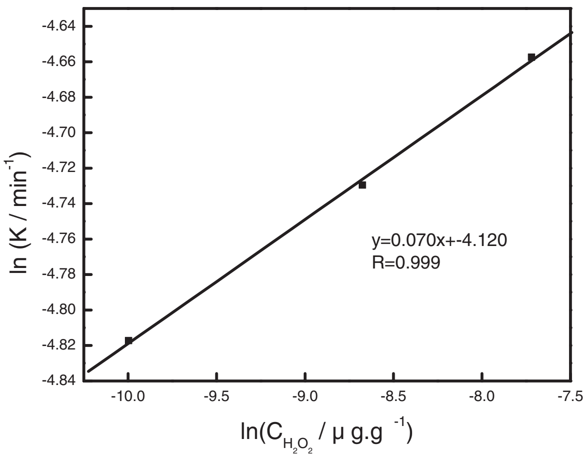


Figure 6. Pseudo-zero-order rate constants for H_2O_2 in the oxidation of thiophene. Reaction condition: TS-1 10gL^{-1}, 333 K, 1 atm, solvent water.

the TS-1 catalyst, the hydrophobic nature of the TS-1 and the minimized diffusive resistance of the substrate in the triphase system [18,19]. This explanation is reasonable. However, it still cannot make it fully clear why thiophene selectively and completely converted to sulfuric acid only when water or *t*-butanol was used as the solvent over TS-1 and why such a reaction does not proceed with formic acid, acetic acid and polyoxyacid as catalyst. On the basis of kinetics study, we propose that the oxidation of aromatic sulfur compounds initiates with the activation of conjugated electrons. There are many arguments about the active species of TS-1. Here, we choose the one proposed by Huybrechts, *et al.* [23], with which thiophene oxidation could be interpreted rationally. It seems that the sequence of thiophene oxidation began with the activation of the electrons on the thiophene ring (scheme 1), followed by the sulfur oxidation once the aromaticity had been destroyed and the thermal cracking of the carbon–sulfur bonds occurred.

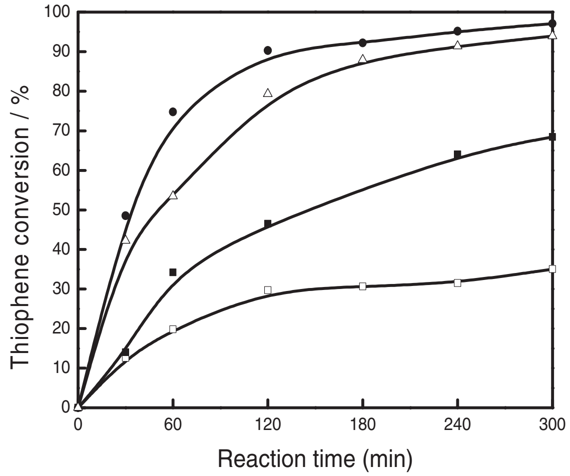


Figure 7. Effect of temperature on thiophene conversion. (□) 293 K, (■) 313 K, (△) 333 K, (●) 353 K.

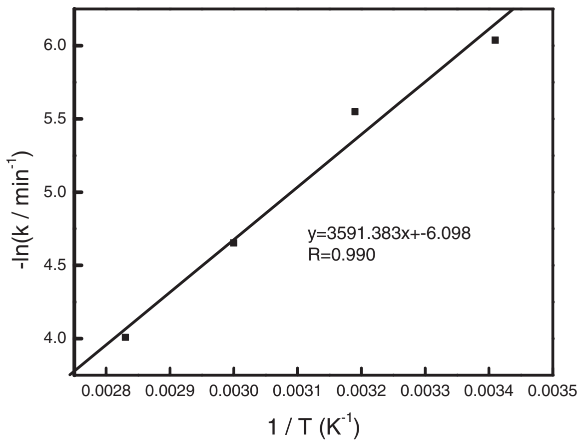
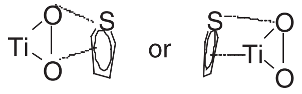


Figure 8. Arrhenius activation energies for thiophene oxidation.



Scheme 1. Postulated species for oxidation of thiophene to sulfuric acid. Catalyst TS-1, Oxidant H_2O_2. Solvent H_2O.

Water does not influence the active site because of the hydrophobic character of the TS-1. *t*-Butanol plays almost the same role as water for its steric hindrance to getting close to the active site of TS-1. When methanol was used as a solvent, no thiophene but octane had been oxidized to the corresponding alcohols and ketones [22,23], since methanol could also coordinate with the active site and then lead the oxidation to another path. Similar results were obtained when acetonitrile was used, except that no oxidation of octane occurred. Neither thiophene nor *n*-octane was oxidized when acetonitrile was used.

4. Conclusion

Thiophene oxidation has been investigated in TS-1/*n*-octane and various solvents. This oxidation reaction can be carried out in solvent water or *t*-butanol because both solvents have difficulty in getting close to the active site and thus do not affect the activation of thiophene. Kinetics parameters most likely reflect that the key step in sulfoxidation of thiophene involves both catalyst and thiophene. Accordingly, it is proposed that the sulfur atom on thiophene will be very easily oxidized by hydrogen peroxide after the 6π-electrons in the thiophene ring are activated by the catalyst. It is promised that the goal of deep desulfurization of gasoline-containing thiophene using the above reaction will be achieved.

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