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Mild oxidation of thiophene over TS-1/H_2O_2

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Abstract

Titanium silicalite (TS-1) is used as catalyst in selective oxidation of thiophene by hydrogen peroxide at 333 K. Fourier transform infrared (FT-IR) and UV–vis characterization shows the presence of framework titanium in all TS-1 samples we prepared with different SiO_2/TiO_2 ratio. Catalytic test over these catalysts confirms that framework Ti species does influence the oxidation of thiophene. The role of non-framework titanium was discussed by studying acid treating of the catalyst. If TS-1 is treated using HCl (2 mol/l) four times, part of the non-framework titanium species will be washed off and the activity of the catalyst increases greatly. These results suggest that framework titanium was crucial for thiophene oxidation. Non-framework titanium is not the active site, but provides steric hindrance for this reaction. Obvious diffusive restriction on the thiophene oxidation was also observed when using TS-1 with different crystal size.

Keywords: Titanium silicalite; Thiophene; Oxidation; Hydrogen peroxide; Oxidative desulfurization

1. Introduction

Deep oxidative desulfurization was considered as one of the most promising alternative desulfurization process to obtain ultra-low sulfur fuels. Organic sulfur compounds such as sulfide, mercaptan, benzothiophene and dibenzothiophene, etc., are very easy to be removed by this oxidative process. However, there is a problem which hindered the application of this new process. In commercial gasoline, large content of organic sulfur are thiophene and its alkyl derivatives. Thiophene was highly stable organic sulfur and cannot be oxidized by hydrogen peroxide under mild conditions. Otsuki et al. [1] reported that the lowest electron density of sulfur atom for sulfoxidation by hydrogen peroxide under mild conditions is between 5.716 and 5.739, while the electron density of sulfur atom in thiophene ring is only 5.696. Therefore, the oxidation of thiophene becomes the key step for oxidative deep desulfurization of gasoline.

Titanium silicalite is a novel catalyst, which is able to catalyze a series of selective oxidations such as aromatic hydroxylations, alkane oxidations, and alkene epoxidations. Recently, several studies have been performed for the catalytic oxidation of organic sulfur compounds over Ti-containing molecular sieves under mild conditions [2–4]. The results show that Ti-containing molecular sieves exhibit good catalytic performance in oxidizing sulfide, mercaptan, benzothiophene, dibenzothiophene, and their corresponding derivatives. No result has been reported about effective oxidation of thiophene. Thus, we focus our study on the thiophene oxidation using TS-1 catalyst [5]. It was shown that thiophene could be oxidized with success when TS-1 was used as catalyst in solvent water or *t*-butanol, while negative results were obtained when applying other catalysts such as acetic acid, formic acid, polyoxometalate. Thiophene also cannot be oxidized over Ti-containing molecular sieves in solvent other than water or *t*-butanol. In order to shed light on the unique role played by TS-1 catalyst in oxidation of thiophene, we further examined the effect of active site of TS-1 on this reaction by studying a series of TS-1 catalyst synthesized at different SiO_2/TiO_2 ratio. The role of different titanium species was studied by comparing the reactivity of TS-1 before and after acid treating. Using TS-1 catalysts with different crystal size provided information of steric effects on the reaction.

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Table 1
Chemical composition of samples prepared with various Ti contents

Sample	SiO_2 (wt.%)	TiO_2 (wt.%)	SiO_2/TiO_2 in gel (mol/mol)	SiO_2/TiO_2 in sample (mol/mol)
a	98.18	–	∞	∞
b	97.76	0.47	256	278
c	97.02	1.00	128	129
d	96.15	1.69	64.0	75.9
e[a]	94.09	3.32	33.3	37.7
f	91.22	7.28	16.0	16.7
g	84.46	13.94	8.0	8.0
h	96.72	1.45	–	49.85

[a] Sample e was treated with 2 mol/l HCl four times.

2. Experimental

2.1. Materials

Thiophene, analytical grade (Parent Medicament Company of China), was used without further treatment. *n*-Octane, analytical grade (Hangzhou refining Company, China), was used as the solvent to dissolve thiophene. Hydrogen peroxide (aqueous solution 30%, Shanghai YuanDa Peroxide Company Ltd., China) was used as oxidant. Its concentration was determined by iodometric titration.

2.2. Catalysts

Titanium silicalite TS-1, was prepared using tetra-propyl ammonium bromide (TPABr) as the template according to reference [6].

2.3. Characterization

Chemical composition of TS-1 with different SiO_2/TiO_2 ratio was analyzed on a Philips PW 1400X spectrometer. Fourier transform infrared (FT-IR) spectra were recorded on a FT-5DX spectrometer, using the KBr pellet technique. UV–vis spectra were obtained on a SHIMADZU UV-240 spectrometer, using silicalite-1 (S-1) as the reference. Morphology of TS-1 was observed on a JEM-1200EX scanning electron microscope (SEM).

2.4. Catalytic activity

In a typical run, the water bath was first heated up and stabilized to the desired reaction temperature (333 K). Then 0.01 ml thiophene was dissolved in 10 ml *n*-octane and added to the water bathed jacket flask equipped with a condenser. About 0.05–0.10 g of the catalyst and 10 ml solvent containing H_2O_2 at H_2O_2/sulfur molar ratio 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 phases were subjected to gas chromatographic analysis with FID detector on a capillary column (SE-54, 15 m × 0.25 mm, 0.33 μm film thickness). Oxidation products were identified through GC (HP-6890)-MS (5973N) analysis.

3. Results and discussion

3.1. Effect of SiO_2/TiO_2 molar ratio

To study the active site for thiophene oxidation, a series of TS-1 catalyst were synthesized at different SiO_2/TiO_2

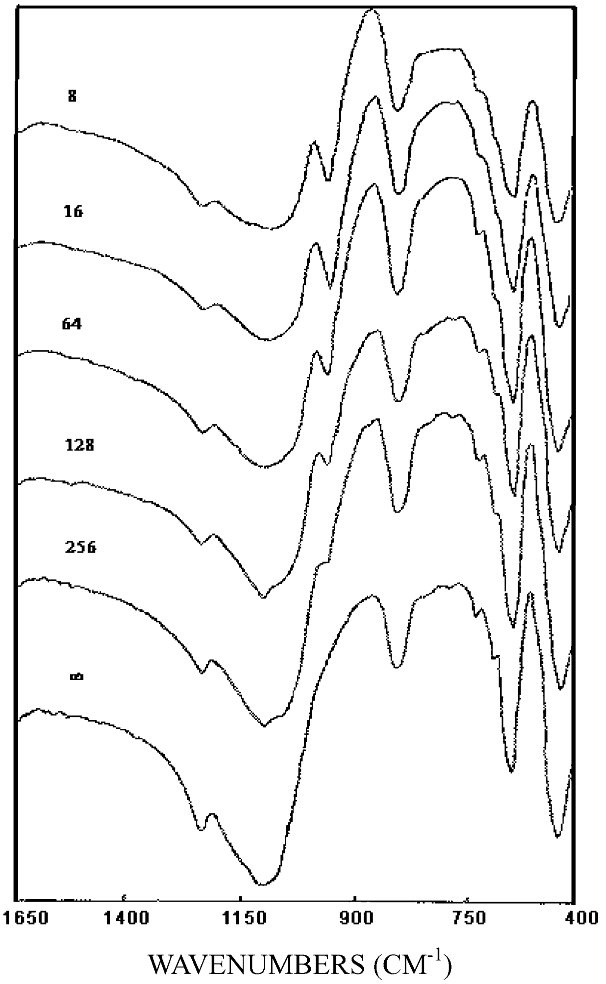

Fig. 1. IR spectra of TS-1 synthesized at different SiO_2/TiO_2.

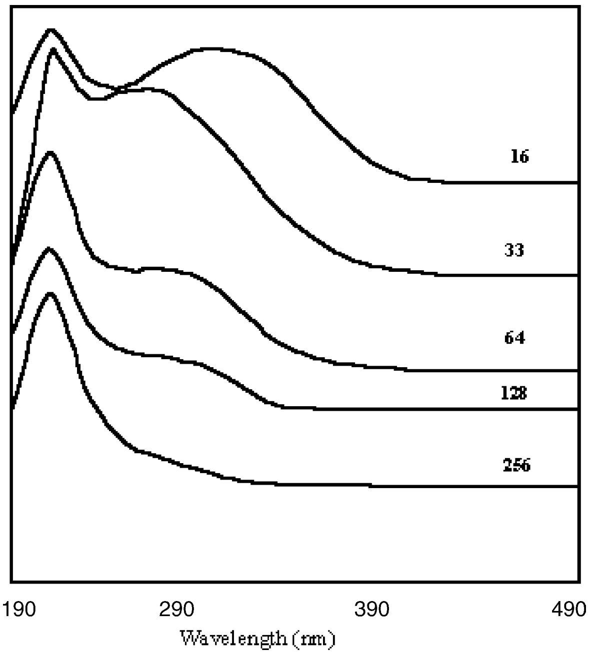

Fig. 2. UV–vis spectra of TS-1 samples with different SiO_2/TiO_2 (S-1 was used as reference).

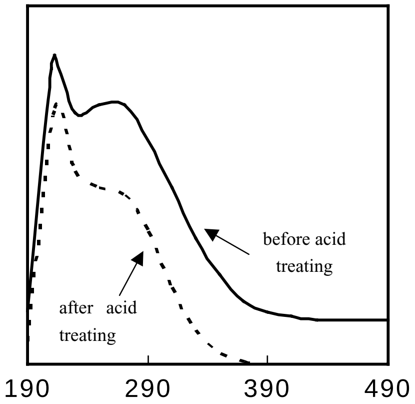

Fig. 4. UV–vis spectra of TS-1 before or after acid treating.

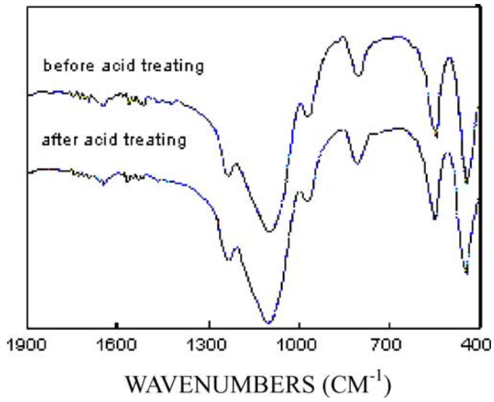

Fig. 5. IR spectra of TS-1 before and after acid treating.

molar ratio. As it shows in Table 1, the titanium content in each catalyst analyzed by XRF is much close to that in gel. FT-IR spectra of these catalysts are shown in Fig. 1, compared with the catalyst without titanium ($SiO_2/TiO_2 = 8$). Each spectrum of the sample with titanium exhibits an absorption band at 960 cm^{-1}, which is assigned to framework titanium of TS-1 [7,8]. A correlation is observed between the intensity of the 960 cm^{-1} band and the framework titanium content. For SiO_2/TiO_2 ratio higher than 16, the band becomes stronger with the decrease of SiO_2/TiO_2 ratio. The band intensity does not change proportionally when further increasing the titanium content in catalyst. The band at 212 nm in UV–vis spectra (Fig. 2) confirmed the presence of isolated Ti species in TS-1 catalyst we prepared [9]. Band

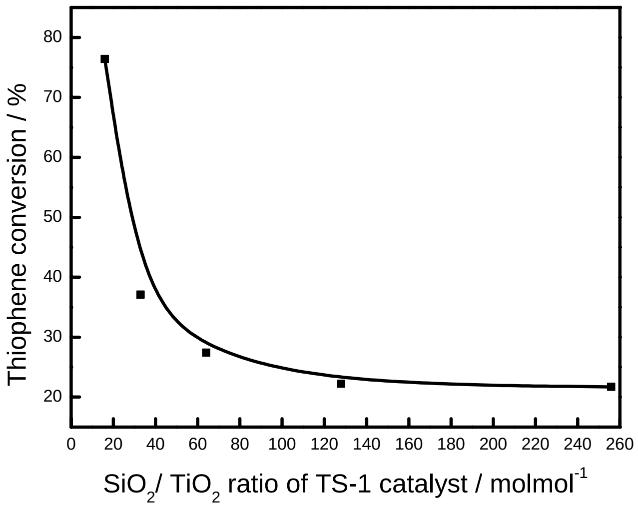

Fig. 3. Catalytic activity of TS-1 with different SiO_2/TiO_2 in oxidation of thiophene. Reaction conditions: temperature, 333 K; reaction time, 30 min; TS-1, 10 g/l; H_2O_2/thiophene = 4:1.

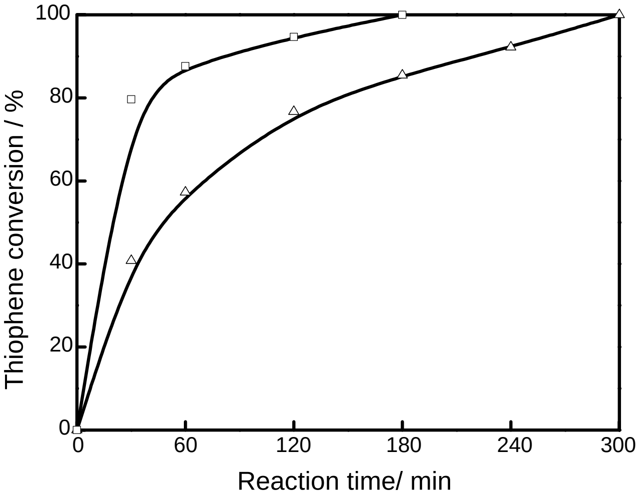

Fig. 6. Effect of acid treating on the performance of TS-1 in oxidation of thiophene. Reaction conditions: temperature, 333 K; TS-1, 10 g/l; H_2O_2/thiophene = 4:1 (mol ratio); solvent, water. (△) sample e, (□) sample h (sample e was treated with 2 mol/l HCl four times).

that appears around 280 nm [10] suggests the presence of non-framework titanium species. The intensity of this band also increases with the decrease of the SiO_2/TiO_2 ratio. The oxidation of thiophene was performed on these catalysts at 333 K and the results of thiophene conversion in 30 min were shown in Fig. 3. Catalytic activity was observed, as expected, for all samples containing framework titanium species and thiophene conversion does go up with increasing of the titanium content in catalyst. 76.4% of thiophene has been oxidized in the first 30 min over TS-1 with a SiO_2/TiO_2 ratio of 16. For the catalyst with a SiO_2/TiO_2 of 256, the conversion of thiophene in 30 min falls down to 21.7%.

UV–vis spectrum of TS-1 with SiO_2/TiO_2 of 256 shows the disappearance of the band around 280 nm (Fig. 2), indicating the absence of non-framework titanium. Although, the reaction rate for this catalyst is relatively lower than other catalysts with higher SiO_2/TiO_2 ratio, thiophene can be totally oxidized to undetectable content in 24 h. This result indicates that framework titanium species in the TS-1 catalyst work as the active site for thiophene oxidation.

3.2. Effect of acid treating

Study on effect of acid treating over TS-1 distinguishes the role played by framework titanium content and non-framework titanium content. The titanium content in TS-1 reduced after being treated using 2 mol/l HCl four times (Table 1). The UV–vis spectra (Fig. 4) shows that the band around 280 nm assigned to non-framework Ti species weakened compared with that of the catalyst before acid treating, while the band around 212 nm does not change obviously. IR spectra of the catalyst before and after acid treating were shown in Fig. 5. The intensity of the band at 960 cm^{-1} also does not change accordingly, indicating without the decrease of framework titanium content. These results imply that most titanium species washed off during acid treating of the catalyst was non-framework titanium. The activity in thiophene oxidation over catalyst after acid treating improved remarkably (Fig. 6). Thiophene conversion rise to 79.6% in 30 min, while thiophene conversion over catalyst before acid treating is only 37.1%. It can be concluded that non-framework titanium does not act as active site for thiophene oxidation. On the contrary, they might be responsible for blocking thiophene from getting close to the active titanium site.

3.3. Effect of crystal size

TS-1 catalysts with different crystal size were characterized by SEM (Fig. 7). The average crystal sizes of these samples are 0.3 μm × 0.17 μm × 0.17 μm, 1.17 μm × 0.67 μm × 0.33 μm, 3.0 μm × 1.3 μm × 0.5 μm and 17.2 μm × 9.4 μm × 2.8 μm, respectively. Obvious difference in reaction rate of thiophene oxidation was observed

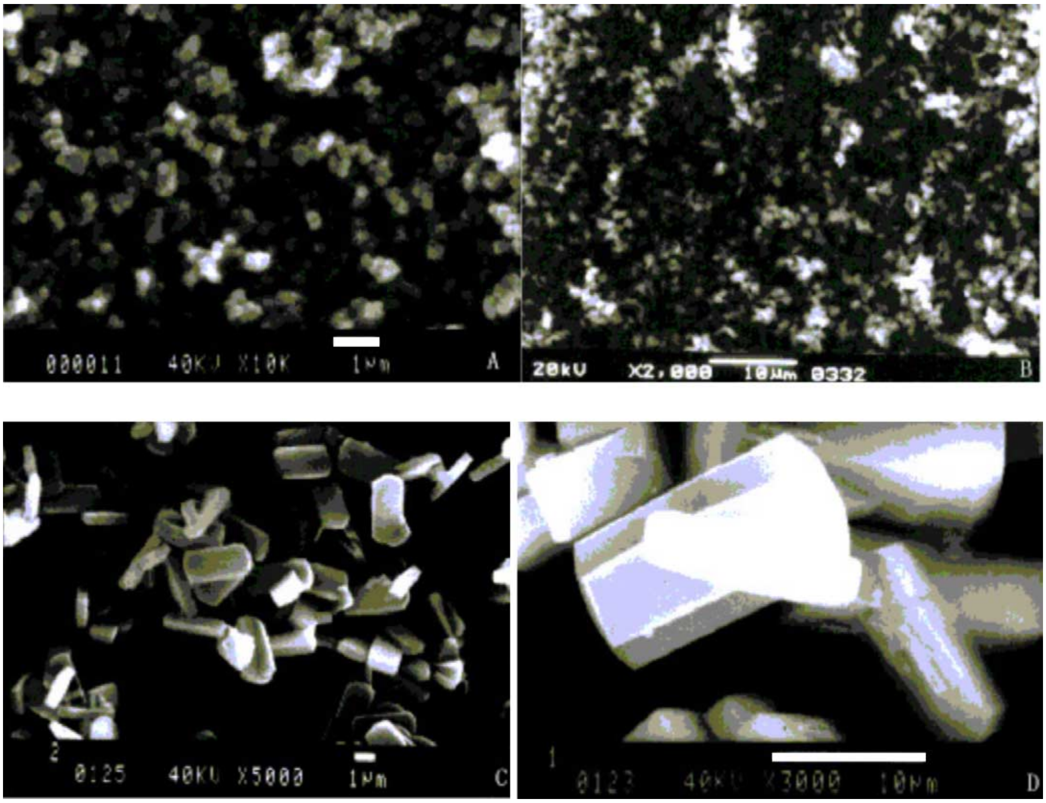

Fig. 7. SEM photographs of TS-1 with different crystal size. (A) ×10 K, 0.3 μm × 0.7 μm × 0.17 μm; (B) ×2000, 1.17 μm × 0.67 μm × 0.33 μm; (C) ×5000, 3.0 μm × 1.3 μm × 0.5 μm; (D) ×3000, 17.2 μm × 9.4 μm × 2.8 μm.

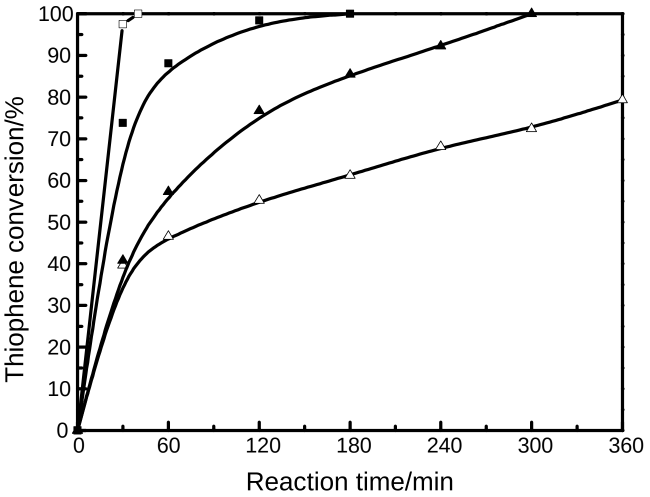

Fig. 8. Effect of crystal size on the performance of TS-1 in oxidation of thiophene. Reaction conditions: temperature, 333 K; TS-1, 10 g/l; H_2O_2/thiophene = 4:1 (mol ratio); solvent, water. (□) sample A; (■) sample B; (▲) sample C; (△) sample D.

over these catalysts (Fig. 8). The reaction rate improved largely as the crystal size of the catalysts diminished. Thiophene conversion reached 97% in 30 min for catalyst with an average crystal size of 0.3 μm × 0.7 μm × 0.17 μm (sample A). It comes to a conclusion that steric hindrance mainly accounts for lower reaction rate over larger crystal catalyst.

4. Conclusions

Although thiophene was commonly considered as impossible to be oxidized by hydrogen peroxide under mild conditions [4], Titanium silicalite was proved to be an effective catalyst for the oxidation of thiophene in solvent water. Framework titanium species is the active site for thiophene oxidation. Conjugated π-electrons on thiophene ring are responsible for thiophene stability. The unique role played by framework titanium might be that they can interrupt conjugation during the reaction. This breakage of the aromaticity of thiophene ring is critical for oxidation of thiophene by hydrogen peroxide under mild conditions. Non-framework titanium in the catalyst is not the active site for thiophene oxidation, and their presence only hindered the reaction. Steric obstacle was also observed by using TS-1 with different crystal size as the catalysts.

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