

Mild Oxidation with H₂O₂ over Ti-Containing Molecular Sieves—A very Efficient Method for Removing Aromatic Sulfur Compounds from Fuels

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This contribution relates a new application of Ti-containing molecular sieves as catalysts for the oxidation of aromatic sulfur compounds with hydrogen peroxide under mild conditions. The catalytic activity of TS-1 (titanium silicalite), Ti-beta, and Ti-HMS (hexagonal mesoporous silica) in the oxidation of thiophene derivatives with hydrogen peroxide was studied. While TS-1 demonstrated low activity due to restricted access of reactants into the porosity, Ti-beta and Ti-HMS proved effective under various reaction conditions, both in two-phase, solid–liquid, and in three-phase, solid–liquid–liquid, systems. The aim of the study was also to obtain information on the applicability of the oxidation method for the removal of organic sulfur compounds from fuels. Results show that the sulfoxidation reaction can be used for decreasing the sulfur content of kerosene without consumption of hydrogen and use of high pressure equipment. In this new method the polyaromatic sulfur compounds (benzo- and dibenzothiophene derivatives) are oxidized into their corresponding sulfoxides and sulfones which are then removed by simple liquid–liquid separation. © 2001 Academic Press

Key Words: thiophene; benzothiophene; dibenzothiophene; kerosene; oxidation; hydrogen peroxide; TS-1; Ti-beta; Ti-hexagonal mesoporous silica.

INTRODUCTION

Sulfur compounds are particularly undesirable in liquid hydrocarbon fuels. Their presence has been associated with corrosion of refining equipment and with premature breakdown of combustion engines. Sulfur also poisons many catalysts that are used in the refining or catalytic conversion of gaseous effluents. Moreover, the atmospheric emission of sulfur combustion products contributes to acid rain, ozone, and smog generation.

In the petroleum refining industry, catalytic hydrodesulfurization (HDS) is currently used for reducing the sulfur

content of the liquid products. However, this process is not cheap for several reasons. One of them is the hydrogen pressure needed for kinetic and catalyst stability purposes. Another reason is related to benzothiophene or dibenzothiophene compounds that constitute very refractory molecules in the process, resulting in significant difficulty in achieving the very low sulfur content presently required in the liquid fuels.

To eliminate undesirable sulfur compounds or to convert them into more innocuous forms, various processes, different from HDS, have been employed, for instance physical extraction with a liquid, selective adsorption on suitable materials, reductive and oxidative microbial processes, or catalytic oxidation. In the latter case, various types of oxidants, including nitrogen oxides, nitric acid, hydrogen peroxide, ozone, *t*-BuOOH, oxygen, air, peracids, etc., are used. The liquid oxidation process with H₂O₂ produces oxidized compounds that can be physically separated and may be easily downstream processed. The oxidation of thiophene derivatives with H₂O₂ is known to take place over various catalytic systems, such as HCOOH, CCl_xCOOH (*x* = 1–3), CF₃COOH (1), CF₃COOH (2), methyltrioxorhenium(VII) (3), and phosphotungstic acid (4).

In a series of previous papers, we have reported that redox solid catalysts, such as Ti-containing zeolites are very effective for the oxidation of thioethers into sulfoxides and sulfoxides into sulfones using H₂O₂ as the oxidant (5–7). It was therefore likely to expect that these catalysts could also be active in the sulfoxidation of aromatic sulfur compounds, such as thiophenes, benzothiophenes, and dibenzothiophenes, all well known as refractory compounds in the HDS process. To our knowledge, the use of Ti-containing molecular sieves as catalysts in this reaction has not been reported previously.

The aim of the study was two-fold. On the one hand, we studied the oxidation with H₂O₂ of several model molecules in both a two-phase solid–liquid (S–L) system (catalyst (S), homogeneous phase solvent–organic substrate–hydrogen peroxide (L)) and a three-phase solid–liquid–liquid (S–L–L) system (catalyst (S), organic layer

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(L), aqueous layer (L)). On the other hand, we sought to obtain information on the applicability of the oxidation method with hydrogen peroxide over Ti-containing molecular sieves in the selective transformation of the organic sulfur compounds contained in kerosene.

EXPERIMENTAL

Materials

Tetrahydrothiophene (Merck, 98%), phenyl sulfide (Aldrich, 98%), thiophene (Aldrich, 99+%), 2-acetylthiophene (Aldrich, 98%), 2,5-dimethylthiophene (Fluka, 99+%), benzothiophene (Aldrich, 99%), and dibenzothiophene (Fluka, 98+%) were used as organic reagents. Hydrogen peroxide (aqueous solution, 31%) from Prolabo was used as oxidizing agent. Acetonitrile (HPLC grade, SDS), methanol (analytical grade, SDS), ethanol (analytical grade, SDS), *tert*-butanol (99%, Prolabo), and decane (99+%, Aldrich) were used as solvents. The kerosene, a nonhydrotreated product containing 0.13 wt% S, was supplied by Feyzin refinery (Lot No. 13019).

Catalysts

Aluminum- and sodium-free titanium silicalite (TS-1; MFI structure) and Ti-beta (BEA structure) zeolites and mesoporous Ti-HMS (hexagonal mesoporous silica) were used as catalysts in oxidation reactions of thiophenes with H_2O_2 . TS-1 and Ti-beta were synthesized according to the methods reported in Refs. (8) and (9), respectively. The mesoporous Ti-HMS was obtained by coprecipitation of silicate and titanium oxide in the presence of a nonionic surfactant (10). The Ti content in all three catalysts was 1 ± 0.2 mol%. Prior to catalytic tests, the materials were calcined in a flow of dry air at 823 K for 6 h to remove the organic species occluded in the pores.

The composition and properties of the calcined catalysts are summarized in Table 1. All catalysts showed well-defined single-phase X-ray diffraction patterns. The DR-UV-visible spectra of the catalysts are shown in Fig. 1. The presence of a sharp absorption band at low wavelength in the spectra indicates that titanium is incorporated as Ti(IV) in the framework of molecular sieves. The absence of any

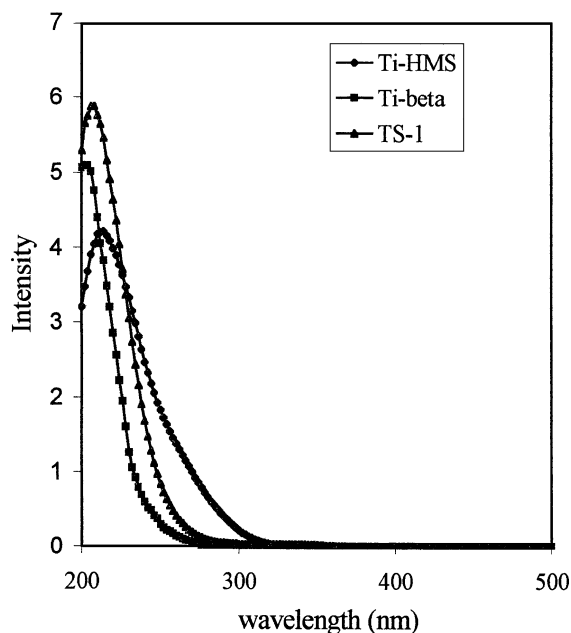


FIG. 1. DR-UV-visible spectra of catalytic materials.

peak in the range 280–360 nm rules out the presence of extraframework TiO_2 species.

Catalytic Experiments

The catalytic sulfoxidation of sulfur-containing organic compounds with hydrogen peroxide was carried out in a 100-mL glass batch reactor, equipped with a magnetic stirrer, a thermometer, and a condenser. In a typical experiment, the solid catalyst was suspended under stirring (750 rpm) in a mixture containing an organic substrate, a solvent, and H_2O_2 at a constant temperature.

The organic compounds were recovered after filtration and, eventually, decantation and analyzed qualitatively by GC-MS and quantitatively by GC-FID equipped with a silicone capillary column (HP-5, poly(5% diphenyl-95% dimethylsiloxane, 25 m \times 0.2 mm, 0.33- μ m film thickness). The hydrogen peroxide was measured by standard iodometric titration.

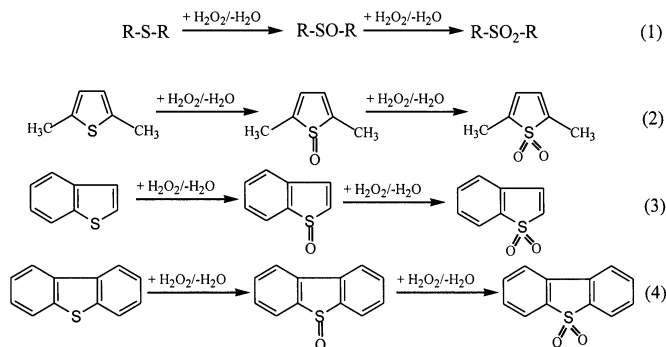
RESULTS AND DISCUSSION

Oxidation of Model Compounds in Two-Phase Solid-Liquid System

It is well known that organic sulfides, thiophenes, benzothiophenes, and dibenzothiophenes are the major sulfur-containing compounds present in liquid hydrocarbon fuels. A series of experiments was carried out to react various organic sulfur compounds in the H_2O_2 -Ti-containing molecular sieves oxidation system. The reactions were carried out in the presence of an organic solvent fully miscible

TABLE 1
Properties of Catalytic Materials

Catalyst	Ti/(Ti + Si) (mol/mol)	BET surface area (m^2/g)	Crystal size (μm)	Pore volume (mL/g)	Size of main channel (nm)
TS-1	0.009	455	0.4	0.22	0.53×0.56
Ti-beta	0.008	470	0.3	0.28	0.76×0.64
Ti-HMS	0.011	838	10	0.42	4

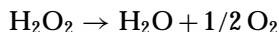


SCHEME 1

with the substrate and the hydrogen peroxide solution, forming a single liquid phase (S-L system).

Under the experimental conditions mentioned above, the oxidation reaction of sulfides and aromatic sulfur compounds by hydrogen peroxide led to the corresponding sulfoxides (1-oxides) and sulfones (1,1-dioxides) as major products (Scheme 1). The selectivity based on hydrogen peroxide consumed was 85–95% for TS-1 and Ti-beta and 75–80% for Ti-HMS catalyst.

A direct decomposition of H₂O₂ was also observed under our experimental conditions.



This was confirmed by carrying out the reaction over the same catalysts in the absence of any substrate. In the absence of any catalyst the oxidation reaction and hydrogen peroxide decomposition did not occur to a measurable extent.

The oxidation results, such as conversion of the sulfur compound, sulfone/sulfoxide ratio, and H₂O₂ selectivity, highly depend on the type of catalyst, nature of substrate or solvent, and molar ratio of reagents. The influence of these factors is examined in the first sections of this paper.

Selection of the Catalyst

The success of TS-1, the original titanium silicalite, as a commercial oxidation catalyst, has prompted a flurry of interest in the area of transition metal-containing zeolites, and, thus, a large number of Ti-containing molecular sieves have been prepared. TS-1 is a remarkable catalyst only for the oxidation of small organic molecules able to enter the channels of the MFI structure. This is not the case of Ti-beta and Ti-mesoporous materials, which are supposed to catalyze the oxidation of bulkier substrates.

The catalytic performance of the three solid catalysts has been studied first in the oxidation reaction of 2,5-dimethylthiophene (2,5-DMT), chosen as a model molecule. The oxidation reaction was carried out at 333 K, using MeCN as a solvent. Results are plotted in Fig. 2.

Under similar conditions, the order of catalyst activity was TS-1 > Ti-beta > Ti-HMS. Since the three solids contained nearly equivalent amounts of framework Ti, these results suggest a higher intrinsic activity of the Ti atoms in TS-1 than in Ti-beta and Ti-HMS. Literature data also indicates that Ti-beta and Ti-mesoporous materials showed lower intrinsic activity toward reactions involving oxidation of small organic molecules as compared to TS-1 (11–13).

In order to determine the influence of pore size of the catalysts in thiophenes oxidation we selected 2,5-DMT, benzothiophene (BT), and dibenzothiophene (DBT), as model substrates. Figure 3 shows the conversions of thiophene derivatives after 1 h of reaction over the three catalysts, under the above-mentioned conditions.

The absence of any activity in sulfoxidation of BT and DBT over TS-1 indicates clearly that these molecules hardly penetrate the TS-1 pores (three-dimensional channel system with 0.53 × 0.56-nm aperture), contrasting with the large-pore Ti-beta (0.76 × 0.64 nm) and mesoporous Ti-HMS (4 nm).

In the case of sulfoxidation of BT, which can penetrate the pores of Ti-beta, the activity of this catalyst is higher than the activity of Ti-mesoporous material, Ti-HMS. On the contrary, when a larger molecule, such as DBT was oxidized, Ti-beta proved slightly less active than Ti-HMS, suggesting that the DBT diffusion can be limited in the 12-member ring pores of Ti-beta zeolite.

Taking this into account, it is clear that of the three tested catalysts, only Ti-beta and Ti-mesoporous materials are able

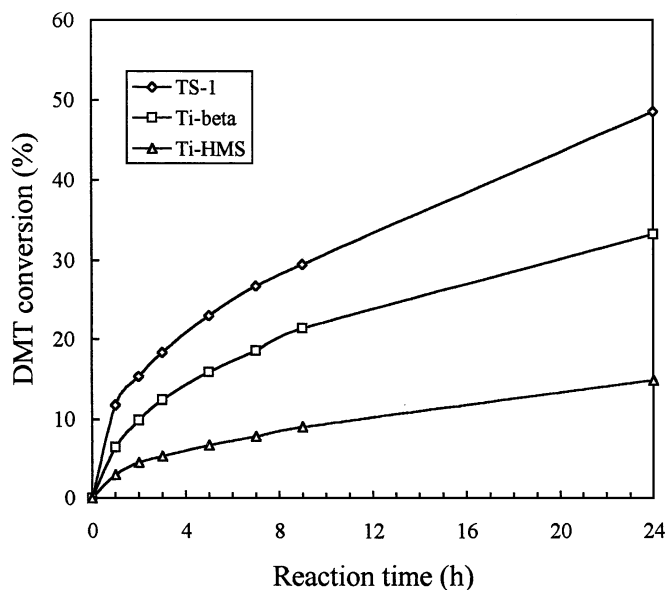


FIG. 2. Oxidation of dimethylthiophene (DMT) with H₂O₂ as a function of reaction time over various catalysts. Conditions: C₀(DMT) = 64.51 × 10⁻³ M, H₂O₂/DMT = 2.4/1 (mole ratio), C_{catalyst} = 3.22 g/L, solvent = acetonitrile, T = 333 K.

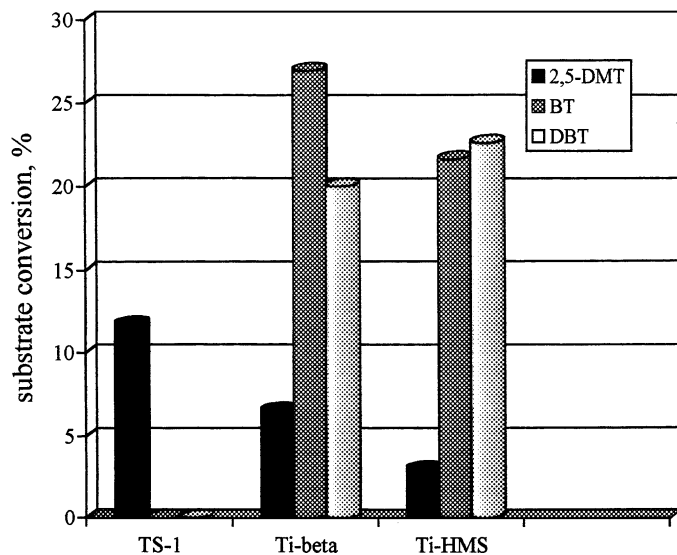


FIG. 3. Influence of catalyst type on the conversion of thiophene derivatives. Conditions: $C_0 = 64.51 \times 10^{-3}$ M, H_2O_2 /substrate = 2.4/1 (mole ratio), $C_{\text{catalyst}} = 3.22$ g/L, solvent = acetonitrile, $T = 333$ K.

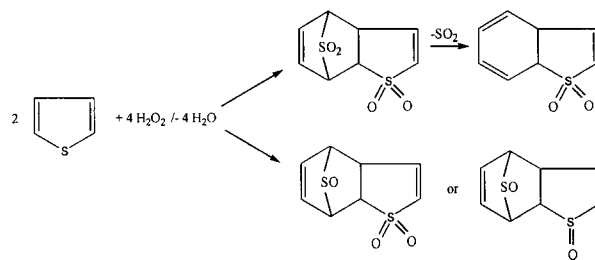
to catalyze the sulfoxidation of polyaromatic sulfur compounds with H_2O_2 . For this reason these solids were used as catalysts for further investigations.

Reactivity of Different Sulfur Species

In a previous contribution (5) reporting the sulfoxidation of thioethers by hydrogen peroxide over Ti-zeolites it was shown that the substrate reactivity is related to both the nucleophilic character of the sulfur atom and to the size of the molecule. Several sulfide and thiophene species, such as tetrahydrothiophene, phenyl sulfide, thiophene, acetylthiophene, 2,5-DMT, BT, and DBT, were therefore oxidized under the following conditions: substrate concentration = 0.0645 M, catalyst concentration = 3.22 g/L, hydrogen peroxide/substrate = 2.4/1 (mol/mol), reaction temperature = 333 K, catalyst = Ti-beta, solvent = acetonitrile.

Under the above conditions, the oxidation reaction of 2,5-DMT, BT, and DBT led directly to the corresponding sulfone, even for low levels of conversion of the substrate. Only traces of sulfoxides were found among the oxidation products. In the case of the alkyl and aryl sulfides, sulfoxide formation proceeds much faster than sulfone formation, and both sulfoxide and sulfone are oxidation products. In the case of thiophene the reaction led to dimer compounds, as depicted in Scheme 2. The thiophene sulfoxide or thiophene sulfone were not detected in the products.

In general, thiophene 1-oxides and 1,1-dioxides that do not contain substituents at ring positions 2 and 5, such as thiophene oxides themselves, undergo facile Diels-Alder cycloaddition, in which one molecule acts as a di-



SCHEME 2

ene and another as a dienophile, to produce sesquioxides (14).

The kinetics of the oxidation of the above-mentioned sulfur compounds are shown in Fig. 4. The results plotted in this figure lead to the following comments:

- Sulfides are oxidized much faster than thiophene derivatives.
- Among the sulfides, tetrahydrothiophene (THT, an alkyl sulfide) is more easily oxidized than diphenyl sulfide (PhSPh, an aryl sulfide).
- The thiophenes are oxidized at different rates depending on their structure: the condensed aromatic thiophenes (BT and DBT) are more reactive than thiophene and substituted thiophene. The oxidation of acetylthiophene (2-AcTh) occurs to a negligible extent (it is to be noted that acetyl is an electron-withdrawing substituent).

These results show that the reactivity of aromatic sulfur compounds in the oxidation with H_2O_2 over Ti-containing molecular sieves contrasts with that observed in the hydrodesulfurization process. For comparison, Table 2 reports the relative reaction rates for various thiophene derivatives in the oxidation and HDS reactions. It appears that the sulfur compounds such as BT and DBT, which are hard to treat by HDS, are readily oxidized with H_2O_2 under mild reaction conditions.

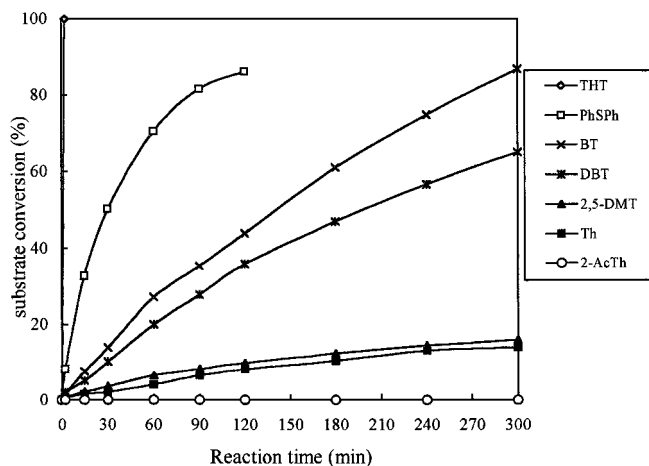


FIG. 4. Kinetics of the oxidation reaction of sulfur compounds with H_2O_2 over Ti-beta, at 333 K, in MeCN as solvent.

TABLE 2

Oxidation and HDS Reactivity of Thiophene Derivatives

Method	Conditions	Relative rate constants Th : BT : DBT	References
Oxidation with H ₂ O ₂	Ti-beta; MeCN; 333 K	1 : 5 : 3.5	This work
HDS	CoMo/Al ₂ O ₃ ; 573 K; 7–10 MPa	22.5 : 13.3 : 1	15

Solvent Effect

The nature of the solvent plays a very important role in the catalytic reactions carried out in the liquid phase, and the results obtained in the oxidation of organic substrates with H₂O₂ over Ti-containing molecular sieves confirm this assertion (16). The solvent has an important effect on the outcome of the reaction, i.e., on yields, by-product formation, and reaction kinetics, although this effect is strongly dependent on the catalyst type and the nature of the substrate.

In order to investigate the solvent effect in the sulfoxidation of thiophene derivatives, we have studied the kinetics of benzothiophene oxidation over Ti-beta as catalyst, at 333 K reaction temperature. The reaction was carried out in the presence of an organic solvent, i.e., acetonitrile, methanol, ethanol, or *t*-butanol, which forms a single phase with the substrate and the hydrogen peroxide solution.

The results, reported in Fig. 5, show that an aprotic polar compound such as acetonitrile leads to the best perfor-

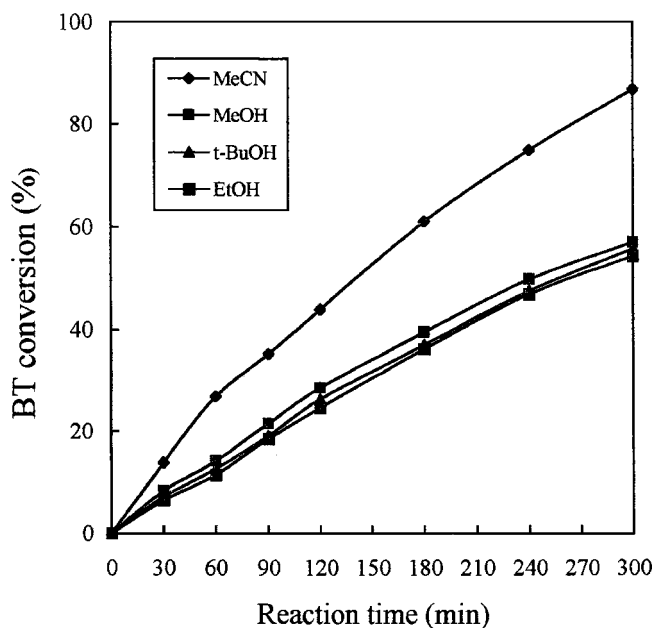


FIG. 5. Kinetics of BT oxidation with H₂O₂ over Ti-beta catalyst at 333 K; C₀ = 64.51 × 10⁻³ M.

mance. The higher reactivity obtained in MeCN with respect to protic solvents, such as MeOH, EtOH, or *t*-BuOH, can be related to the hydrophilic/hydrophobic character or to the acid properties of the catalyst. Ti-beta zeolites contain hydroxyl groups with acidic and hydrophilic character (17). The protic solvent (ROH), H₂O₂, and water (as reaction product) are strongly adsorbed by this material and the inner substrate concentration will be very low, thus hindering catalytic performance. In contrast to the hydrophilic character of Ti-beta (and Ti-mesoporous materials), TS-1 has a hydrophobic character. For the later catalyst, methanol or other small protic compounds are the preferred solvents for oxidation reactions (6, 13, 18). The favorable effect of the MeCN in the oxidation reactions over Ti-beta catalyst was also associated with the poisoning of the acid sites by basic molecules of the solvent (19, 20) or with a possible addition reaction of hydrogen peroxide to solvent molecules, leading to the peroxyimidic acid, R-C(=NH)-O-OH, which is known to be an active oxidizing agent toward various organic substrates (6).

As can be observed in Fig. 5, in the case of ROH solvents, the activity of Ti-beta is practically independent of the type of alcohol (MeOH=EtOH=*t*-BuOH), indicating that no steric nor electronic effects of these solvents are involved.

Influence of the H₂O₂/Substrate Ratio

All the above experiments were carried out with a H₂O₂/BT ratio of 2.4. The effect of the variation of H₂O₂ to substrate ratio has been studied by using BT as organic reagent, acetonitrile as solvent, and Ti-beta as catalyst. The reaction was performed at 333 K and the results obtained are shown in Fig. 6. The BT conversion increases sharply with increasing H₂O₂ concentration. Thus, after 2 h of reaction, the BT conversion increased from 21 to 76.5% as the ratio of H₂O₂/BT increased from 1.2 to 9.6.

In order to determine the kinetic order with respect to the BT concentration, we considered the case of a large excess of oxidant (H₂O₂/BT = 9.6/1). Under these conditions, one can assume that the hydrogen peroxide concentration is constant and the general rate equation of the oxidation of BT over Ti-beta,

$$r = d[\text{BT}]/dt = k \cdot [\text{BT}]^a \cdot [\text{H}_2\text{O}_2]^b \cdot [\text{Catal.}]^c,$$

can be simplified to the form

$$r = K \cdot [\text{BT}]^a,$$

where *a*, *b*, *c*, are the partial orders in BT, H₂O₂, and catalyst, respectively, and $K = k \cdot [\text{H}_2\text{O}_2]^b \cdot [\text{Catal.}]^c$.

A linear dependence of the ln[BT] versus reaction time is found (Fig. 7), which is characteristic for a first-order versus the organic substrate.

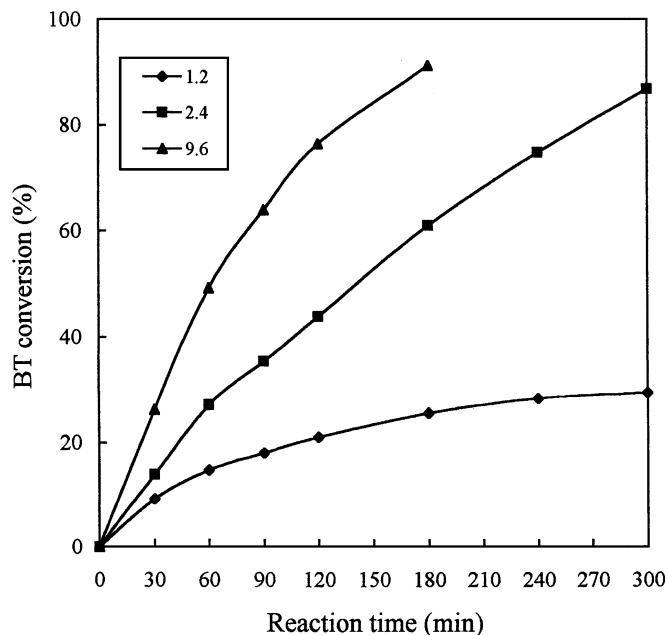


FIG. 6. Effect of the $\text{H}_2\text{O}_2/\text{BT}$ ratio on BT conversion. Conditions: $C_0 = 64.51 \times 10^{-3} \text{ M}$, $C_{\text{catalyst}} = 3.22 \text{ g/L}$, solvent = acetonitrile, $T = 333 \text{ K}$.

Oxidation of Model Compounds in Three-Phases S-L-L System

We also investigated the oxidation of some thiophenes with H_2O_2 in a three-phase S-L-L system: catalyst (S), an organic layer consisting of the substrate dissolved in *n*-decane (L), and an aqueous layer containing a polar solvent and 30% H_2O_2 (L). Initially all the thiophenes were in *n*-decane, in due course the oxidation products (sulfones) were transferred in the polar solvent.

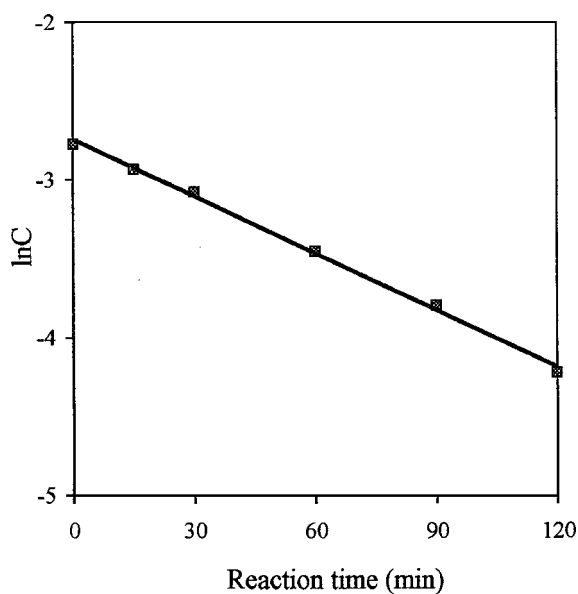


FIG. 7. First-order plot for the conversion of BT over Ti-beta.

TABLE 3

Conversion of BT and DBT in Three-Phase S-L-L System Oxidation.^a

Catalyst	Solvent	% Conversion of	
		BT	DBT
Ti-HMS	Acetonitrile	56.0	67.0
Ti-beta	Acetonitrile	96.7	91.0
Ti-beta	Methanol	100	93.7
Ti-beta	Water	64.3	25.0

^a Reaction time, 5 h.

The oxidation reaction of two thiophene derivatives, BT and DBT, was carried out over Ti-beta and Ti-HMS catalysts using acetonitrile, methanol, or water as polar solvents. The solid catalyst (100 mg) was thoroughly stirred with 0.5 mmol of BT, 0.5 mmol of DBT, 20 mL of *n*-decane, 20 mL of polar solvent, and 1 mL of aqueous 30% H_2O_2 at 343 K. After the reaction the phases were separated and analyzed.

The overall conversion of BT and DBT after 5 h of reaction under these conditions is presented in Table 3. The results lead to the following remarks:

- Ti-beta is a very active catalyst for the oxidation of both BT and DBT in presence of an organic polar solvent.
- Ti-mesoporous material shows lower activity as compared to Ti-beta under similar conditions.
- Water is a poor solvent in three-phase system oxidation.

The solvent performances depend on the solubility of the sulfone oxidation products in the reaction mixture. Thus, the oxidized organic sulfur compounds are fully soluble in acetonitrile and methanol and only partially soluble in water.

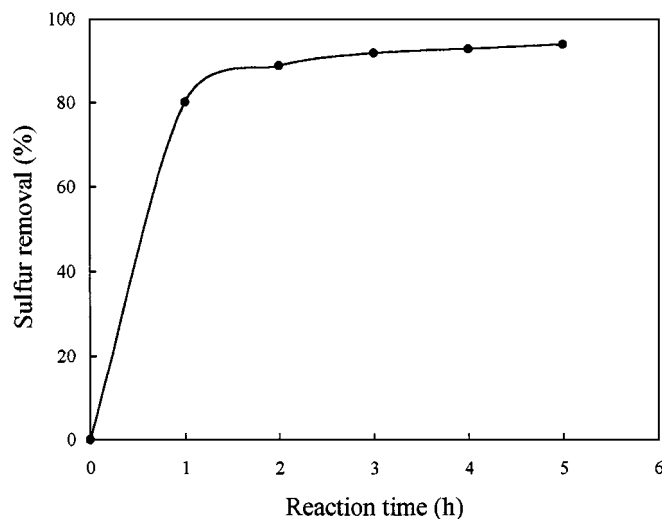


FIG. 8. Kinetics of the removal of sulfur from kerosene at 333 K.

TABLE 4

Influence of Catalyst and Nature of the Solvent on the Sulfur Removal from Kerosene. (*T* = 343 K)

Catalyst	Solvent	Reaction time (h)	Phase	Sulfur (ppm)	Sulfur removal (%)
—	Acetonitrile	Extraction	Kerosene	1220	7.0
Ti-HMS	Acetonitrile	9	Kerosene	190	85.5
Ti-HMS	Acetonitrile	9	Acetonitrile	2500	
Ti-beta	Acetonitrile	5	Kerosene	80	94.0
Ti-beta	Acetonitrile	5	Acetonitrile	2300	
Ti-beta	Ethanol	5	Kerosene	390	70.2
Ti-beta	Ethanol	10	Kerosene	300	77.0
Ti-beta	Ethanol	24	Kerosene	250	81.0
Ti-beta	Ethanol	24	Kerosene ^a	80	94.0
Ti-beta	Ethanol	24	Ethanol	1800	
Ti-beta	Water	10	Kerosene	840	36.0
Ti-beta	Water	10	Kerosene ^a	300	77.1
Ti-beta	Water	10	Water	450	

^a Kerosene washed with acetonitrile.*Oxidation of Sulfur Compounds from Kerosene*

The removal of sulfur from petroleum products remains an important task, and the thiophenic sulfur is the most difficult to eliminate. Sulfur compounds in a fuel such as kerosene consist mostly of BT and DBT derivatives. The above results showed that Ti-beta and Ti-HMS were able to catalyze the sulfoxidation reaction of these thiophenes into corresponding sulfones. Taking this into account, it was expected that these catalysts were also active in the oxidation of sulfur compounds from kerosene with hydrogen peroxide.

Experimentally, the straight-run kerosene was mixed with a suitable solvent, such as acetonitrile or ethanol, which are immiscible with the kerosene, but in which the oxidized sulfur compounds readily dissolve. In the first experiment, 1 g of Ti-beta was intensively stirred with 40 mL kerosene (1310 ppm sulfur), 20 mL acetonitrile, and 0.35 mL hydrogen peroxide (30 wt% in water) at 333 K, under atmospheric pressure. The kinetic of removal of sulfur from kerosene is presented in Fig. 8. After 2 h of reaction, the extent of removal of the organic sulfur compounds from kerosene amounted to 90% in terms of total sulfur.

The oxidation of kerosene with H₂O₂ was also investigated under other reaction conditions. Thus, in a 100-mL glass batch reactor, 200 mg of catalyst was stirred with 40 mL kerosene (1310 ppm sulfur), 20 mL solvent (acetonitrile, ethanol, or water), and 2 mL hydrogen peroxide at 353 K. At the end of the runs the solutions were analyzed for residual H₂O₂. The peroxide efficiency was 90 ± 2% for Ti-beta and 80 ± 2% for Ti-HMS. The combined effects of catalyst, solvent, and reaction time on sulfur removal from kerosene are summarized in Table 4.

As shown in Table 4, both Ti-beta and Ti-HMS catalysts exhibited remarkably high activities in the removal of sulfur

compounds from kerosene by mild oxidation with H₂O₂. The best results were obtained using acetonitrile as polar solvent because the oxidized compounds are fully soluble in this solvent, while they are only partially soluble in ethanol and water.

CONCLUSIONS

We have investigated the sulfoxidation reaction of aromatic sulfur compounds with hydrogen peroxide over Ti-containing molecular sieves. It has been shown that the large-pore catalytic materials, such as Ti-beta and mesoporous Ti-HMS, are active for the selective oxidation of thiophene derivatives to the corresponding sulfones, whereas the medium-pore zeolite TS-1 is totally inactive in the oxidation of polyaromatic sulfur compounds with H₂O₂. It has been also shown that thiophenes are less reactive than thioethers.

The sulfoxidation reaction with hydrogen peroxide can be used as an interesting method for removing sulfur from kerosene without hydrogen consumption and high pressure equipment utilization (21). The best results were obtained using acetonitrile as polar solvent, in the presence of both Ti-beta and Ti-HMS as catalysts.

During the chemical treatment, the oxidized organic sulfur compounds transfer integrally in the polar solvent, which is immiscible with the kerosene. The oxidized product can therefore be removed by a simple liquid-liquid separation.

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