Cyclodimerisation and cyclotrimerisation during the ring-opening reactions of ethylene sulfide (thiirane) over acidic molecular sieves and alumina

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The transformations of ethylene sulfide were studied at three reaction temperatures (423, 473 and 523 K) on different acidic molecular sieves (HZSM-5, HY and AlMCM-41) and alumina in a pulse system. The main reaction pathways were found to be desulfurisation, cyclo-oligomerisation, the latter being more important. In this reaction channel mainly direct dimer (six-membered ring: 1,4-dithiane) and trimer (1,4,7-trithiacyclononane) formation occurred. The former product was always predominant, however, 1,4,7-trithiacyclononane was also significant, especially on molecular sieves with larger pore openings and alumina. At elevated temperatures 2-methyl-1,3-dithiolane (a five-membered cyclic molecule) was also detected. This molecule was formed in the highest amount on HZSM-5 among the catalysts applied revealing that a more constrained environment is advantageous for this dimerisation type to occur.

KEY WORDS: thiirane; acidic molecular sieves; alumina; cyclo-oligomerisation; desulfurisation; 1,4-dithiane; 1,4,7-trithiacyclononane; 2-methyl-1,3-dithiolane; pulse system

1. Introduction

Three-membered rings generally are very reactive, yet they are relatively easy to prepare. Therefore, further functionalisation of compounds is very often performed first transforming it to cyclopropane (cyclopropanation) or oxirane (epoxidation) derivative, then opening up the ring by nucleophiles and/or electrophiles. Literature concerning the preparation of these ring systems and their further transformations is vast (for reviews, see, *e.g.*, [1,2]). Many papers describe observations regarding the laws governing the ring-opening reactions of cyclopropanes and oxiranes either in the homogeneous or the heterogeneous phase. Reactions in the homogeneous phase may be of direct interest to synthetic chemists working in the laboratory, while those taking place on solid materials may be of interest beside synthetic organic chemists to those working in fine chemical industry as well. Furthermore, these reactions are interesting from the catalytic chemist's point of view, since a relatively wide variety of reactions can be studied under model conditions, yet bearing the promise of applications on the larger scale.

In view of the facts detailed above it is surprising that investigating the chemical properties of thiirane, a three-membered system with sulfur heteroatom in the ring, is a neglected area of research. Its ring-opening reactions even in the homogeneous phase were scarcely studied [3–6] and those on solid acid catalysts are simply no man's land. It is awesome, because potentially thiirane derivatives bear all the advantages why cyclopropane and oxirane derivatives are so frequently applied. They are easily synthesised, yet stable enough enabling easy handling, yet should be reactive enough to serve as synthon in preparing more complicated functionalised molecules. They also may provide access to sulfur-containing heterocycles. Since the reactions of thiirane and its derivatives were not described on solid acids before, mapping possible transformation pathways and assessing the reactivity of the ring are of value not only to a catalytic chemist studying model systems but also to those working in the fine chemical industry and to purely synthetic organic chemists as well.

During previous investigations with oxygen-containing three-membered ring systems (methyloxirane and stereoisomeric 2,3-dimethyloxiranes [7–9]), we found that beside acid catalyzed single ring opening of the C–O bonds, dimerisation leading to dioxolane and dioxane derivatives took place on acidic molecular sieves. Using the experiences collected in these studies we decided to extend our research efforts to the sulfur-containing three-membered ring. Results obtained are reported in this contribution.

2. Experimental

The molecular sieves used were HZSM-5 (Si/Al = 13.8), HY (Si/Al = 30) and AlMCM-41 (Si/Al = 40). The alumina was obtained from Haldor Topsøe.

The H-zeolites were prepared by wet ion exchange starting from the Na forms. Four-fold ion-exchange was per-

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Table 1
Characterising data of the catalysts.

Zeolite	d_{001}[a] (nm)	BET surface areas (m^2/g)	Brønsted/Lewis sites[b]
HZSM-5	–	336	0.88
HY	–	604	8.67
AlMCM-41	4.059	932	0.62
Alumina	–	232	0.33

[a] Calcined samples.
[b] Calculated on the basis of IR spectra of adsorbed pyridine.

formed in 1 mol/dm^3 aqueous NH_4NO_3 solution. The duration of one exchange was 12 h and it was carried out at ambient temperature. Then, the resulting ammonium forms were deammonised by calcination in vacuum for 6 h at 873 K.

The MCM-41 derivatives were synthesised in our laboratory following recipes published in [16–19]. Sodium silicate and aluminium isopropoxide were the silica and aluminium sources, respectively. Hexadecyltrimethylammonium bromide was the surfactant, NaOH and sulfuric acid solutions were used for adjusting the pH. The resulting gel was crystallised for 6 days under autogenous conditions at 373 K. Then, it was filtered and washed by distilled water, dried at 373 K and, finally, calcined at 773 K for 10 h to burn the template off.

Thiirane (ethylene sulfide) is a commercially (Fluka) available compound and was used as received. Hydrogen was produced in a Matheson generator.

The samples were characterised by powder X-ray diffractometry, BET surface area measurements and FT-IR spectroscopy.

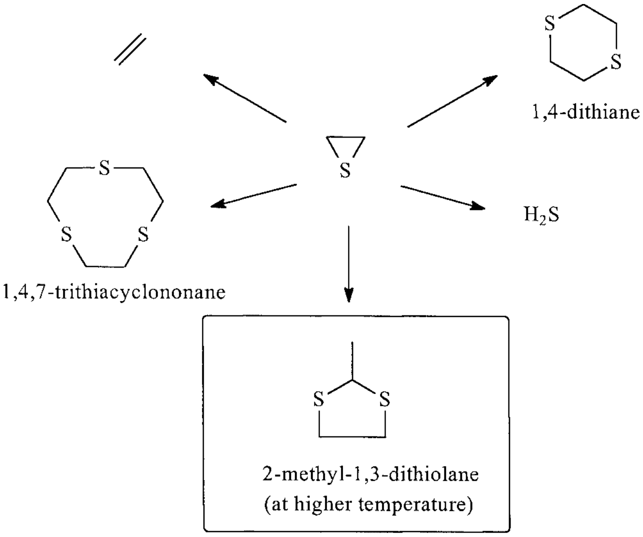
X-ray diffractograms were registered on well-powdered samples with a DRON 3 diffractometer in order to check crystallinity and to determine d_{100} distances for the MCM-41 sample.

BET measurements were performed in a conventional volumetric adsorption apparatus at the temperature of liquid nitrogen (77.4 K). Prior to measurements the samples were pretreated in vacuum at 573 K for 1 h.

The acid–base properties were studied by pyridine adsorption followed by IR spectroscopy (Mattson Genesis I FT-IR spectrometer, 128 scans for one spectrum, WIN-IR software package). Self-supported wafers (10 mg/cm^2 thickness) were pressed from the zeolite samples. They were pretreated in the optical cell at 573 K for 2 h in vacuum. 1.33 kPa of pyridine was adsorbed on the activated samples at 363 K for 1 h followed by cooling to room temperature under continuous evacuation. Bands at 1540 and 1450 cm^{-1} were used for calculating Brønsted and Lewis acidities, respectively.

Characteristic data on the aluminosilicates collected by the different methods are displayed in table 1.

The reactions of ethylene sulfide were studied in a pulse reactor system applying hydrogen as carrier (45 cm^3/min gas flow). The reaction temperature ranged from 423 to 523 K. The size of the pulse was 1 μl and 20 mg of catalyst was used. The following pulse sequence was applied for each catalyst: three consecutive pulses at 423 K, then, a pulse at 473 K and the fifth pulse at 523 K; 30 min was allowed to elapse between the pulses. Blank experiments (experiments without catalysts) have been performed at the temperatures applied in catalytic experiments and no transformations of thiirane have been found.



Scheme 1. Transformation pathways during the ring opening of thiirane on solid acids.

Analysis of the product mixture was done by a GC-MS system (Hewlett–Packard (HP) 5890 gas chromatograph equipped with a HP 5970 quadrupole mass selective detector). Good separation was achieved on a 50 m long CP-WAX 52CB coated CHROMPACK WCOT fused silica capillary column by applying a temperature program (303 K for 15 min, 323 K for 20 min and 473 K for 10 min). Product identification was based on the NBS/NIH/EPA/MSDC database and clean samples.

3. Results

As far as the overall transformation is concerned, throughout the pulse sequence the order of conversion on the same amount of catalyst was as follows: HY > AlMCM-41 > alumina > HZSM-5. Desulfurisation, dimerisation and trimerisation with the formation of 1,4-dithiane and 1,4,7-trithiacyclononane, respectively, were the main transformation pathways. Most of the sulfur, which was removed during desulfurisation, was desorbed as hydrogen sulfide (this occurred mainly on HY), however, certain amount could remain attached to the zeolite surface.

The major transformation pathways are depicted in scheme 1.

On HZSM-5, in the first pulse (423 K) desulfurisation occurred: ethylene and H_2S were produced. Beside this reaction, on the other catalysts, already the first pulse resulted in a cyclic dimer (1,4-dithiane) and in smaller but significant amount the cyclic trimer (1,4,7-trithiacyclononane). Cyclodimerisation was even the main transformation pathway

Table 2
Composition of the reaction mixture in the ring-opening and cyclo-oligomerisation reactions of thiirane on acidic molecular sieves and alumina (pulse system with 1 μl pulse size, 45 cm^3/min H_2 as carrier, 20 mg catalyst, 423 K reaction temperature).

Catalyst	Pulse No.	Composition (mol%)				
		Thiirane	H_2S	Ethylene	1,4-dithiane	1,4,7-trithiacyclononane
HZSM-5	1	76.6	4.4	19.0	0	0
	2	91.3	0.6	2.2	4.8	1.1
	3	94.8	0	0.3	4.0	0.9
HY	1	2.5	1.4	16.2	78.6	1.3
	2	6.4	2.7	10.9	78.8	1.2
	3	6.4	2.7	10.9	78.4	1.6
AlMCM-41	1	10.9	0.4	12.3	66.8	9.6
	2	13.5	0.3	12.7	62.1	11.4
	3	14.9	0.3	12.7	61.7	10.4
Alumina	1	16.6	0	5.0	77.3	1.1
	2	44.3	0.1	2.5	52.2	0.9
	3	60.1	0.1	1.1	37.9	0.8

on these catalysts and its proportion remained steadily high on subsequent pulses on HY and AlMCM-41. Alumina was gradually deactivated on subsequent pulses although even in the third pulse it remained significantly more active than HZSM-5 in the first pulse and produced more dimers than HZSM-5 in its most active state toward this transformation pathway. The dimer and the trimer appeared in the second pulse on HZSM-5 too. The 1,4-dithiane became the major product and the selectivity towards 1,4,7-trithiacyclononane was higher than it was, *e.g.*, on AlMCM-41. The yield, however, was the highest on AlMCM-41.

Product distributions at 423 K during three pulses are collected in table 2.

On elevating the temperature after the third pulse at 423 K, naturally, the conversion of thiirane increased and a new cyclic product appeared, 2-methyl-1,3-dithiolane (a compound with five-membered ring). It was first observed on HZSM-5 at as low as 473 K and became significant at 523 K. On the other acidic substances it first appeared at 523 K, however, in very low amount. Interestingly, 1,4,7-trithiacyclononane became the most significant on HZSM-5 compared to the other substances at temperatures higher than 423 K, even if it was not observed at all at 423 K in the first pulse. As a strong tendency, however, 1,4-dithiane remained the most important product at the elevated temperatures too.

Product distribution at 423 K in the third pulse and at the elevated temperatures (473 and 523 K) are collected in table 3.

4. Discussion

Product yields reveal that the conversion level on the solid acids applied here increases with increasing pore diameter (ZSM-5: 5.3 Å × 5.6 Å, HY: 7.4 Å, AlMCM-41: 40.6 Å). Since the major products are cyclic compounds with six or nine heavy atoms in the cycle, molecules clearly significantly larger in size than thiirane, larger space is expected to be advantageous for the dimerisation and trimerisation reactions to occur. Experimental observations are in accordance with this expectation. In more constrained environment (HZSM-5) thiirane conversion was smaller and in the first pulse cyclic oligomers were not formed at all. On increasing pore size the yield of 1,4-dithiane and 1,4,7-trithiacyclononane (compounds with six- and nine-membered ring, respectively) dramatically increased verifying that larger inner space is advantageous for the formation of these compounds. On a non-porous catalyst like alumina, the lack of size constraint is reflected on the activity toward dimerisation and trimerisation, however, it is also clear that a three-dimensional pore system is advantageous in maintaining close to steady activity of the catalysts.

Oxygen and sulfur are close in their properties and analogous oxygen- and sulfur-containing compounds are expected to behave similarly. This expectation is in large part fulfilled when the ring-opening properties of thiirane and methyloxirane catalysed by acidic molecular sieves are compared. Dimerisation producing cyclic compounds is the main transformation pathway for both molecules. However, methyloxirane gives predominantly dioxolane (five-membered ring) derivatives [8,9], while 1,4-dithiane (six-membered ring) is the main product for thiirane dimerisation. At moderate temperature(s) there is no dithiolane (five-membered ring) formation at all. At higher temperatures 2-methyl-1,3-dithiolane appeared but has never become the main dimer.

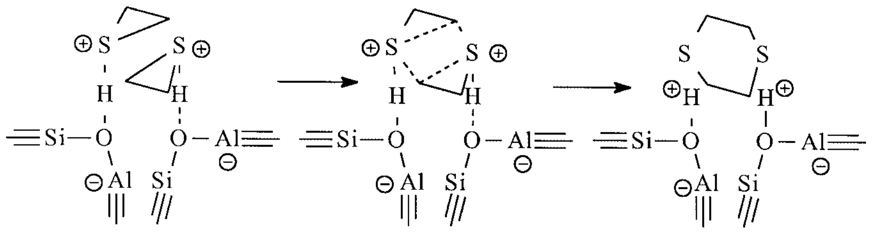
For the formation of the six-membered ring compound larger pores were found to be advantageous, however, dithiolane (compound with five-membered ring) formation, though at higher temperature, was favoured by a more constrained environment, exactly like that of the dioxolane derivatives (compounds with five-membered ring) from the ring opening of methyloxirane.

As far as the mechanism of 1,4-dithiane synthesis is concerned on HZSM-5, C–S bond scission and the formation

Table 3

Composition of the reaction mixture in the ring-opening and cyclo-oligomerisation reactions of thiirane on acidic molecular sieves and alumina at increasing temperatures (pulse system with 1 μl pulse size, 45 cm^3/min H_2 as carrier, 20 mg catalyst, 423, 473 and 523 K reaction temperatures).

Catalyst	Temperature	Composition (mol%)					
	(K)	Thiirane	H_2S	C_2H_4	1,4-dithiane	2-methyl-1,3-dithiolane	1,4,7-trithiacyclononane
HZSM-5	423	94.8	0	0.3	4.0	0	0.9
	473	2.9	0.1	24.3	48.7	0.6	23.4
	523	22.6	0.2	28.2	21.2	4.5	23.5
HY	423	6.4	2.7	10.9	78.4	0	1.6
	473	1.0	2.0	5.3	90.6	0	1.1
	523	2.9	3.3	12.3	79.3	0.5	1.7
AlMCM-41	423	61.7	0.3	12.7	61.7	0	10.4
	473	9.8	0.4	6.0	70.3	0	14.1
	523	11.0	0.5	6.2	61.6	0.9	19.8
Alumina	423	60.1	0.1	1.1	37.9	0	0.8
	473	14.6	0.1	1.4	76.4	0	7.5
	523	7.3	1.9	3.0	77.0	1.1	9.7



Scheme 2. Mechanistic suggestion for cyclodimerisation producing 1,4-dithiane.

of new C–S bonds is thought to occur in sequence. Part of the first pulse is suggested to remain adsorbed on the zeolite and the second pulse combines with the adsorbed moieties providing with the sulfur-containing heterocycles. On the other catalysts (HY, AlMCM-41 and alumina), however, since cyclodimers and cyclotrimers appear in the first pulse and they keep close to steady concentration on subsequent pulses in the larger pore zeolitic substances, the events probably take place in concerted way or in a very rapid sequence. A schematic representation of 1,4-dithiane formation is depicted in scheme 2.

As far as the active sites are concerned, we have no reason to believe that either the Brønsted or the Lewis centres are exclusively responsible for the transformation to occur. Rather, it is thought that any of the observed reaction may proceed on any of these acid sites.

5. Conclusions

Whatever the accurate reaction mechanism is, acidic molecular sieves proved to be good catalysts for transforming thiirane and possibly their derivatives. At the same time thiiranes are proved to be nearly as reactive and versatile reagents as their oxygen-containing counterparts.

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