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Chemistry

R. D. Obolentsev and V. I. Dronov

1960

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Abstract

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KINETICS OF THE CONVERSION OF CERTAIN MONOCYCLIC SULFIDES OVER AN ALUMINOSILICATE CATALYST

(Presented by Academician A. V. Topchiev on 7 VII 1959)

In connection with the growth in the production and processing of sulfurous and high-sulfur petroleum, the study of transformations of organosulfur compounds occurring during catalytic cracking is of not only theoretical but also great practical interest. The literature contains information ([1–3]) on schemes of conversion of organosulfur compounds over an aluminosilicate catalyst, but information on the kinetics of these transformations is almost entirely lacking. The aim of the present investigation was to fill this gap in part.

We studied the kinetics of conversion over an aluminosilicate catalyst of the cis and trans isomers of 2,5-dimethylthiophane and 2,5-di-*n*-propylthiophane, 2-ethylthiophane, 2-*n*-hexylthiophane, 2-methylthiacyclohexane, thiacycloheptane, and 2-ethylthiophene. The experiments were carried out in a flow-type laboratory apparatus under atmospheric pressure at temperatures of 350, 400, and 450°C and at volumetric feed rates of the feedstock to the catalyst from 1 to 80. The sulfides were taken in the form of 0.45% (with respect to sulfur) solutions in benzene and in several other solvents. As catalyst we used a spherical aluminosilicate catalyst with an "activity index" of 33. The hydrogen sulfide formed in the reaction was absorbed by a 10% solution of cadmium chloride and determined iodometrically. Total sulfur in the catalyzates was determined by the lamp method, mercaptan sulfur by the method of Borgstrom and Reid, and sulfide sulfur from the difference between total and mercaptan sulfur; in some experiments, it was determined by potentiometric titration and from the ultraviolet absorption spectra of iodine complexes. Sulfur contained in the coke was trapped during regeneration of the catalyst in the form of sulfur dioxide and determined iodometrically. For each experiment a material balance for sulfur was compiled. On the basis of the results of experiments carried out to study the kinetics of conversion of monocyclic sulfides over an aluminosilicate catalyst, we established that hydrogen sulfide is the principal sulfur-containing product of these transformations. The amount of mercaptan sulfur in the catalyzates does not exceed 2.5%, calculated on the sulfur contained in the initial feedstock. The amount of sulfur in the coke does not exceed 3% of the sulfur contained in the initial solution.

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For the kinetic characterization of the transformations of cyclic sulfides studied by us, we used the equations proposed in general form by Frost ([1,4]) and Kazeev ([2,5])

$$\alpha + \beta v_0 y = v_0 \ln \frac{1}{1-y}, \tag{1}$$

where v_0 is the volumetric feed rate of sulfide (in mmol per 1 g of catalyst per hour); y is the depth of desulfurization (in fractions of unity); α and β are parameters.

$$\ln \frac{m}{D-m} = a\tau^b, \tag{2}$$

where τ is the nominal contact time in seconds; m is the depth of desulfurization (in %); D is the limiting value of m as $\tau \to \infty$; a and b are parameters.

The conventional contact time (τ) was calculated from the equation

$$\tau = \frac{v_p\, 273.16 \cdot 760}{nTP \cdot 22415}, \tag{3}$$

where v_p is the volume of the reaction space (in cm^3), n is the number of moles of feed passing through the reactor per 1 sec; T is the absolute temperature; P is the pressure (in mm Hg).

The values of the parameters of the kinetic equations found by us are summarized in Table 1. For all cyclic sulfides and 2-ethylthiophene studied by us

Table 1

Parameters of the kinetic equations

Cyclic sulfides	T_r, °C	α	β	a	b	D
cis-2,5-Dimethylthiophane	350	0,21	1,00	0,90	0,71	90
cis-2,5-Dimethylthiophane	400	0,50	0,99	1,66	0,71	94
cis-2,5-Dimethylthiophane	450	1,49	1,01	3,42	0,71	95

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Cyclic sulfides	T_r, °C	α	β	a	b	D
cis-2,5-Dimethylthiophane over catalyst with grain size 0.05 cm	400	1,79	1,00	4,27	0,73	94
trans-2,5-Dimethylthiophane	350	0,20	0,98	0,91	0,67	89
trans-2,5-Dimethylthiophane	400	0,65	1,00	2,00	0,70	94
trans-2,5-Dimethylthiophane	450	1,44	0,99	2,94	0,66	94
2-Ethylthiophane	350	0,17	0,76	0,65	0,89	82
2-Ethylthiophane	400	0,42	0,74	1,33	0,88	84
2-Ethylthiophane	450	1,08	0,77	2,71	0,85	90
2-Methylthiacyclohexane	350	0,11	0,98	0,65	0,67	81
2-Methylthiacyclohexane	400	0,26	0,97	1,06	0,69	94
2-Methylthiacyclohexane	450	0,73	0,98	2,12	0,70	94
Thiacycloheptane	350	0,10	0,74	0,41	0,84	78
Thiacycloheptane	400	0,35	0,74	1,08	0,84	82,5
Thiacycloheptane	450	0,77	0,72	2,11	0,86	87
2-*n*-Hexylthiophane	350	0,15	1,02	1,04	0,59	78
2-*n*-Hexylthiophane	400	0,78	1,00	2,29	0,66	92
2-*n*-Hexylthiophane	450	2,15	0,97	4,95	0,72	93,5

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Cyclic sulfides	T_r, °C	α	β	a	b	D
cis-2,5-*n*-Propylthiophane	300	0,08	1,00	0,64	0,54	76
cis-2,5-*n*-Propylthiophane	350	0,41	1,00	1,44	0,66	87
cis-2,5-*n*-Propylthiophane	400	1,27	1,01	2,61	0,60	92
cis-2,5-*n*-Propylthiophane	450	2,57	1,00	4,44	0,62	95
trans-2,5-di-*n*-propylthiophane in solvents: benzene	350	0,63	0,91	1,64	0,63	87
trans-2,5-di-*n*-propylthiophane in solvents: cetane	400	0,80	1,00	1,16	0,63	92
trans-2,5-di-*n*-propylthiophane in solvents: decalin	400	0,76	0,94	1,37	0,64	92

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Figure 1

Figure 1: Figure 1

Cyclic sulfides	T_r, °C	α	β	a	b	D
trans-2,5-di-*n*-propylthiophane in solvents: α-methylnaphthalene	400	1,36	0,99	2,14	0,63	92
2-Ethylthiophene	450	0,02	1,00	0,19	1,05	30
2-Ethylthiophene	500	0,06	0,97	0,21	1,12	36
2-Ethylthiophene	550	0,06	0,99	0,28	1,05	38

the extents of conversion were calculated as a function of contact time at temperatures of 350, 400, and 450°C. As an example, in Fig. 1 such a dependence is presented for the temperature 450°.

It is evident from Fig. 1 that the experimental points are satisfactorily located relative to the calculated curves. At short contact times a difference is observed in the average rates of conversion of cyclic sulfides. The rate of conversion increases with increasing molecular weight of the sulfide. The rate of conversion of 2-alkylthiophanes is lower than that of the isomeric 2,5-dialkylthiophanes, but this difference is smoothed out for high-molecular-weight sulfides. The rates of conversion of isomeric five- and six-membered cyclic sulfides are practically identical and higher than those for seven-membered sulfides. At a temperature of 350°

the rates of conversion of cis- and trans-2,5-dimethylthiophanes are practically identical; at 450° the rate of conversion of the cis isomer is somewhat higher than that of the trans isomer, but at 400° the reverse dependence is observed. As the contact time increases, the difference in the average conversion rates of the sulfides we studied decreases and, at 450°, reaches the highest values for thiacyclopentane and 2-ethylthiophane, 87-90%, and for the others

Fig. 1. Solid lines—calculated curves for the degree of conversion of cyclic sulfides at 450°C as a function of contact time. The dashed line is the curve of the relationship between contact time and space velocity. 1—2-ethylthiophene;

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Figure 2

Figure 2: Figure 2

Fig. 3

Figure 3: Fig. 3

2—thiacyclopentane; 3—2-ethylthiophane; 4—2-methylthiacyclohexane; 5—trans-2,5-dimethylthiophane; 6—cis-2,5-dimethylthiophane; 7—2-hexylthiophane; 8—trans-2,5-di-n-propylthiophane.

94-95%. The difference in the rates of conversion of cyclic sulfides in the presence of an aluminosilicate catalyst is undoubtedly reflected in the composition of the cyclic sulfides contained in the distillate products of catalytic cracking, which become enriched in low-molecular-weight

Fig. 2. Calculated curves for the degree of conversion of trans-2,5-di-n-propylthiophane at 400°C as a function of the diluents and contact time. Solvents: 1—cetane; 2—decalin; 3—α-methylnaphthalene; 4—benzene.

sulfides and 2-alkylthiophanes as a result of depletion in high-molecular-weight sulfides and 2,5-dialkylthiophanes. It has been shown that the aluminosilicate catalyst can be used for the selective removal of monocyclic sulfides from their mixtures with thiophenes.

The aluminosilicate catalyst has a highly developed surface and pores of small diameter. In this connection, we studied the kinetics of conversion of cis-2,5-dimethylthiophane at 400° on catalysts with an average grain size of 0.25 and 0.05 cm and, by the method proposed by Rozovskii and Shchekin (6), calculated the diffusion-inhibition factors. The diffusion-inhibition factor for the conversion of cis-2,5-dimethylthiophane in the presence of a catalyst with a grain size of 0.25 cm proved to be 0.22,

and for conversion on the more finely divided catalyst, 0.79. Consequently, in the first case the conversion of cis-2,5-dimethylthiophane proceeds in the intradiffusion region, and in the second case—in the transition region. In view of the fact that the organosulfur compounds contained in petroleum products subjected to catalytic cracking are represented to a considerable extent by cyclic sulfides, it must be assumed that distillates with the lowest sulfur content should be obtained during cracking in a suspended bed with a powdered catalyst.

Fig. 3. Depth of conversion of cis-2,5-dimethylthiophane dissolved in an isooctane-isooctylene mixture as a function of the isooctylene content. Points—experimental data.

To determine the influence of the fractional and group hydrocarbon composition of petroleum products undergoing cracking on the sulfur content in the cracking products, we studied the kinetics of conversion of trans-2,5-di-n-propylthiophane

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Fig. 4

Figure 4: Fig. 4

at 400° in various solvents (Fig. 2). From examination of the curves presented in the figure it follows that trans-2,5-di-*n*-propylthiophane dissolved in benzene and α-methylnaphthalene is converted at the highest rate. The lowest conversion rate is observed for trans-2,5-di-*n*-propylthiophane dissolved in cetane. Study of the conversion of cis-2,5-dimethylthiophane dissolved in an isooctylene–isooctane mixture showed that the depth of conversion of cis-2,5-dimethylthiophane decreases markedly with increasing isooctylene content in the mixture (Fig. 3). The results obtained show that the sulfur content in distillate products of catalytic cracking should depend on the fractional and group hydrocarbon composition of the petroleum products being cracked.

Fig. 4. Calculated curve of the total depth of conversion of four cyclic sulfides. Points—experimental data.

As a result of studying the kinetics of conversion of a mixture of cyclic sulfides consisting of cis-2,5-dimethylthiophane, 2-ethylthiophane, 2-methylthiacyclohexane, and thiacyclopentane, it was shown that the total depth of conversion of the sulfide mixture obeys the rule of additivity (see Fig. 4). This fact is of fundamental importance, since it testifies to the possibility, from data on the composition of the sulfide mixture contained in the petroleum products being cracked and their kinetic characteristics, of determining the degree of desulfurization.

Bashkir Branch
Academy of Sciences of the USSR

Received
6 VII 1959

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