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OXIDATIVE DEHYDROGENATION OF ALKYLHETEROAROMATIC COMPOUNDS.

2*. DEHYDROGENATION OF ALKYLTHIOPHENES

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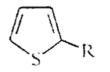
The dehydrogenation of a series of alkylthiophenes has been studied on vanadium–magnesium systems in the presence of atmospheric oxygen, and on zinc–chromium oxide catalysts in the absence of oxygen. Optimum conditions have been determined for bringing this about enabling vinylthiophenes to be obtained in high yield and with high selectivity. The advantages of the oxidative dehydrogenation method have been shown in the synthesis of vinyl derivatives of thiophene.

Vinylthiophene and its homologs are known as antioxidants and selective extractants. They readily polymerize and are used as copolymerization products with butadiene, styrene, and its halogen derivatives [1]. The polymers obtained possess high softening temperatures and good dielectric properties [2].

Multistage methods of obtaining vinylthiophenes are known [3], but information on obtaining them by dehydrogenation is sparse [4].

We have studied the dehydrogenation of 2-alkyl-thiophenes (Ia-d) on vanadium–magnesium oxide systems in the presence of atmospheric oxygen and also high temperature dehydrogenation with zinc–chromium oxide catalyst (in both cases dilution with water vapor was used).



I a-d

I a R = Et, b R = Pr, c R = *i*-Pr, d R = Bu

Samples used for the investigation were vanadium–magnesium catalyst of the composition optimal for carrying out the oxidative dehydrogenation of alkylpyridines [5] and alkylaromatic hydrocarbons [6], and zinc–chromium catalyst effective in the dehydrogenation of alkylaromatic compounds [7].

We have shown that methylthiophene and thiophene were contained in small amounts in the reaction products in addition to the main target products, viz. vinylthiophene and the initial compounds (I). No formation of oxygen-containing products was observed. The process was little complicated by side decomposition reactions, the content of unsaturated hydrocarbons in the outlet gases was no more than 0.2-0.8%. Carbon formation on the catalyst surface was absent and the content of carbon dioxide in the outlet gases was 6-12%.

Data are given in Table 1 on the oxidative dehydrogenation of alkylthiophenes (Ia-d) on vanadium–magnesium catalyst. In the case of ethylthiophene (Ia) the yield of 2-vinylthiophene (IIa) was 45% at 380°C and 58-60% at 480-500°C. The selectivity of the process was 81-85%. On dehydrogenating 2-propylthiophene (Ib) the yield of 2-propenylthiophene (IIb) was also high at 56% at 500°C. At 380°C the yield of 2-isopropenylthiophene (IIc) was 44%, and of 2-butenylthiophene (IId) 38%. The ability to convert the compounds investigated into vinyl derivatives fell in the series (Ia) > (Ic) > (Ib) > (Id). Further

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TABLE 1. Oxidative Dehydrogenation of Alkylthiophenes (Ia-d) on Vanadium–Magnesium Catalyst. Catalyst Composition: 10% V_2O_5, 88% MgO, 2% Modifying Additives [5]. Volume Rate 0.25 h^{-1}, Duration of Experiment 5-6 h

Initial compound	T, °C	Molar ratio of (I) : O_2 : H_2O	Vinylthiophene yield (II) in wt.%	
			on (I) passed	on (I) converted
2-Ethylthiophene (Ia)	380	1 : 1,2 : 9	45,0	85,0
	400		50,0	82,0
	450		58,0	81,0
	500		60,0	81,0
2-Isopropylthiophene (Ic)	380	1 : 1,2 : 8	44,0	79,0
2-Propylthiophene (Ib)	380	1 : 1,1 : 9	42,0	78,0
	500		56,0	75,0
2-Butylthiophene (Id)	380	1 : 1,0 : 10	38,0	75,0

TABLE 2. Dehydrogenation of Alkylthiophenes (Ia) and (Ib) to 2-Vinylthiophene (IIa) and 2-Propenylthiophene (IIb) on Zinc–Chromium Catalyst. Catalyst Composition: 80% ZnO, 15% Cr_2O_3, 5% Modifying Additives. Duration of Experiment 1.5-2.0 h

T, °C	Volume rate h^{-1}	Molar ratio (I) : H_2O	Yield of (II), wt.%	
			on alkylthiophene passed	on alkylthophene converted
		2-Ethylthiophene (Ia)		
500	0.30	1 : 14	46,0	87,0
500	0,15	1 : 14	47,0	76,0
550	0,25	1 : 14	52,0	86,0
600	0,25	1 : 14	60,0	82,0
600	0,25	1 : 7	48,0	78,0
600	0,25	1 : 28	58,0	85,0
		2-Propylthiophene (Ib)		
500	0,25	1 : 28	41,4	84,0
500	0,15	1 : 28	42,0	76,0
530	0,25	1 : 28	49,6	83,5
600	0,26	1 : 28	55,8	83,0
600	0,26	1 : 28	56,0	83,4

oxidation was observed in the reverse sequence (Id) > (Ib) > (Ic) > (Ia). The catalyst operated in a stable manner, no carbon formation on the catalyst surface and no reduction in activity when using an air–oxygen mixture were observed during the experiments (5-6 h).

The conversion of thiophene over vanadium–magnesium catalyst was also investigated to determine the stability of the thiophene ring under the conditions of oxidative dehydrogenation. The elemental composition of the catalyzate (C, H, S), determined by analytical methods, was close to that calculated for the initial thiophene. Hydrogen sulfide was not detected among the gaseous products. Consequently the thiophene ring is stable under the oxidative dehydrogenation conditions.

From investigations carried out previously on the preparation of vinylaromatic and vinylpyrdine compounds [5-7], it follows that oxidative dehydrogenation has significant advantages over dehydrogenation without a hydrogen acceptor even on such an effective catalyst as zinc–chromium. It seemed expedient to study the dehydrogenation of alkylthiophenes over zinc–chromium catalyst as well for comparison.

Data are given in Table 2 on the dehydrogenation of the alkylthiophenes (Ia) and (Ib) on zinc–chromium oxide catalyst. A reduction in the molar ratio of water vapor to 1:7 (1:1 by weight) leads to a significant reduction in the selectivity of the process, a reduction in the yield of the corresponding vinylthiophenes (II), and also to carbon deposition on the catalyst. Similar results were also obtained on reducing the volume rate of supply of raw material to 0.15 h^{-1}. It must be noted that replacement of water vapor by carbon dioxide leads to a somewhat worse result; the content of unsaturated hydrocarbons in the contact gas rose to 2.0-2.4%, probably due to cracking. The yields of 2-vinylthiophene (IIa) and of 2-propenylthiophene (IIb) remained at 50-52%. The activity of the catalyst remained constant during 10-15 h continuous operation, no surface carbon formation was observed. The optimum dehydrogenation conditions on the zinc–chromium oxide catalyst are therefore: temperature of 500-600°C, molar ratio of alkylthiophene: H_2O = 1:14-28, and volume rate 0.25-0.3 h^{-1}. Under these conditions high activity and stability are provided in cycles of dehydrogenation.

The results of the investigations carried out show that the dehydrogenation of alkylthiophenes on zinc–chromium catalyst and their oxidative dehydrogenation on vanadium–magnesium systems enable the corresponding vinylthiophenes to be obtained in up to 60% yield at a selectivity for the process of 85-87%.

It must be noted that the oxidative dehydrogenation method for alkylthiophenes, as in the case of ethylbenzene [6] and alkylpyridines [5], has certain advantages over the usual catalytic dehydrogenation. High conversions and selectivity are achieved at relatively low temperatures, viz. 380-480°C at a low molar dilution with water vapor of 1:10, and a low vapor temperature of 450°C.

It might be suggested from the results of the investigation that the oxidative dehydrogenation of alkylthiophenes occurs on the vanadium–magnesium catalysts at active centers of the same character as were observed for the oxidative dehydrogenation of ethylbenzene [6] and alkylpyridines [5]. These contain vanadium ions of high oxidation states in octahedral coordination with oxygen in closest vicinity.

EXPERIMENTAL

The vanadium–magnesium catalysts were prepared by the batch method from MgO carrier (S_{sp} 100 m^2/g) using an aqueous solution of the calculated quantity of ammonium vanadate [5]. The zinc–chromium catalysts were obtained from zinc and chromium nitrates by precipitation with ammonia [7]. The obtained mass was shaped using a press. Granules were dried in the air and then in a drying chamber. The dried catalyst was subjected to heat treatment in an air stream with a rate of temperature increase of 100°C/h to 550-650°C and was maintained at this temperature for 3-4 h. In the case of the zinc–chromium catalyst, additional activation by dehydrogenation of olefins for 1 h with subsequent regeneration for 30 min was carried out to form its porous structure and complete its phase composition. The maximum activity was achieved after 5-6 cycles of this treatment.

Modifying additives used for the vanadium–magnesium catalyst were $KHSO_4$, $MgSO_4$, ZnO, and CdO (2% in total). Oxides of manganese, cesium, potassium, and aluminum (5% in total) were used for modifying the zinc–chromium catalyst.

A flow-through quartz reactor (volume 40 ml) with a stationary catalyst layer was used to study the catalytic properties.

The reactions were investigated over a wide range of variables: 360-600°C, volume rate 0.15-1.0 h^{-1}, molar ratio of alkylthiophene: O_2:H_2O = 1:0-1.2:7-28. The duration of experiments was 0.5-15 h. Regeneration of the catalyst was carried out after each experiment.

The liquid and gaseous products were analyzed by GLC. The column (2 m × 3 mm) was packed with polyethyleneglycol 2000 on NaCl treated previously with 1% KOH solution. Analysis temperature was 90°C, carrier gas helium. Correction coefficients for estimating from the chromatograms were determined from the analysis of artificially prepared mixtures of the initial and final compounds in various weight ratios.

The yields of vinyl derivatives on the raw material passed through and converted were calculated from the analytical results and material balance data for each experiment.

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