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Influence of the texture of chromia catalysts on their activity in synthesis of 2-methylthiophene

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The texture of Cr_2O_3-K_2O/Al_2O_3 catalysts containing oxides of rare earth elements (REE) was studied. The catalysts are used for the synthesis of 2-methylthiophene by the reaction of H_2S with *n*-pentane or piperilene. The heterocyclization of *n*-pentane is a consecutive reaction involving a step of dehydrogenation of initial hydrocarbon. At this step the texture of the catalyst affects the yield of 2-methylthiophene. The yield of 2-methylthiophene obtained from piperilene and H_2S is independent of the catalyst texture.

Key words: Cr_2O_3-K_2O/Al_2O_3 catalysts, oxides of rare earth elements, heterocyclization, piperilene, *n*-pentane, 2-methylthiophene, hydrogen sulfide, texture.

Chromia catalysts exhibit a high activity in the synthesis of thiophenes from C_4—C_8 hydrocarbons and hydrogen sulfide.[1] The reaction of H_2S with piperilene or *n*-pentane affords 2-methylthiophene. The active Cr_2O_3-K_2O/Al_2O_3 catalyst containing oxides of rare earth elements (REE) has been developed[2—4] for this process. In this work we studied the influence of the catalyst texture on the yield of 2-methylthiophene in the reaction of H_2S with *n*-pentane or piperilene.

Experimental

The Cr_2O_3—K_2O/Al_2O catalysts containing REE oxides, *viz.*, 360-R (**1**)[5] and 445-RB (**2**), were used.

Catalyst **1** had the following composition (wt.%): Cr_2O_3, 5; Polirit (CeO_2, 2.7; La_2O_3, 1.3; Nd_2O_3, 0.75; Pr_2O_3, 0.25), 5; K_2O, 1; Al_2O_3, 89. Alumina γ-Al_2O_3 (A-1 trade mark) (S_{sp} = 249 $m^2\,g^{-1}$) was calcined in air at 500 °C for 3.5 h, impregnated with a solution of Polirit in 13% HNO_3 with addition of H_2O_2, dried for 6 h at 120 °C, and impregnated with aqueous solutions of $K_2Cr_2O_7$ and $(NH_4)_2Cr_2O_7$. The catalyst was then dried and calcined for 10 h at 700 °C.

Catalyst **2** had the same chemical composition as catalyst **1** but γ-Al_2O_3 in the support formulation was partly replaced by α-Al_2O_3 and AlOOH (repricipitated aluminum hydroxide, boehmite). This combined support was developed at the Yarsintez Research-and-Production Association (Yaroslavl, Russia) for the preparation of the catalyst for the commercial dehydrogenation of *n*-butane.[6,7]

The surface area and pore structure of the initial catalysts, dried at 120 °C and calcined at 700 °C, were determined by analysis of the adsorption isotherms of benzene vapor measured gravimetrically at 20 °C. Before adsorption measurements, all samples were evacuated at 400 °C to a constant weight. Specific surfaces were calculated by the BET equation accepting the molecular area of benzene[8] to be 0.41 nm^2. The data on the chemical composition and the texture characteristics of catalysts **1** and **2** before and after calcination are presented in Table 1.

Table 1. Chemical composition and texture characteristics of the chromium oxide catalysts

Catalyst	Chemical composition (wt.%)	Treatment	Texture		
			S_{sp} /$m^2\,g^{-1}$	V /$cm^3\,g^{-1}$	r /nm
1	Cr_2O_3, 5; REE*, 5; K_2O, 1; γ-Al_2O_3, 89	Uncalcined	160	0.43	1.8; 3.3; 5.7
		Calcined	86	0.43	7.5
2	Cr_2O_3, 5; REE*, 5; K_2O, 1; γ-Al_2O_3, 37; α-Al_2O_3, 25; AlOOH,** 27.0	Uncalcined	155	0.18	1.7; 2.8
		Calcined	74	0.20	2.7; 3.8; 5.4

* Composition, wt.%: CeO_2, 2.7; La_2O_3, 1.3; Nd_2O_3, 0.75; Pr_2O_3, 0.25.

** Reprecipitated aluminum hydroxide (boehmite); d = 2.3—2.4 g cm^{-3}, bulk density 0.7—0.8 g cm^{-3}.

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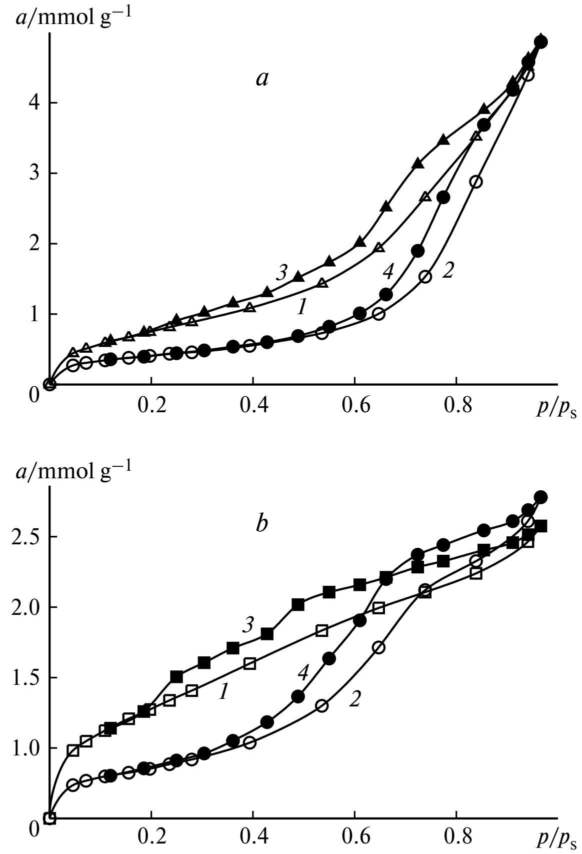


Fig. 1. Isotherms of adsorption (*1*, *2*) and desorption (*3*, *4*) of benzene at 20 °C on catalysts **1** (*a*) and **2** (*b*) for the noncalcined (*1*, *3*) and calcined at 700 °C samples (*2*, *4*).

The pore volume size distribution curves were calculated using the Kelvin equation based on analysis of the desorption branches of the isotherms with a correction for the thickness of the adsorbed film. The experimental curves and calculated parameters of the texture of the samples are presented in Figs. 1 and 2 and in Table 1.

Heterocyclization of *n*-pentane and piperilene by reactions with H_2S was performed in a flow-type reactor. The procedures of the reactions and analysis of the products have been described previously.[5] Piperilene and *n*-pentane (reagent grade) were distilled. Hydrogen sulfide available from the Moscow Oil Processing Plant was purified with monoethanolamine, compressed on cooling with liquid nitrogen, and stored in a stainless steel cylinder.

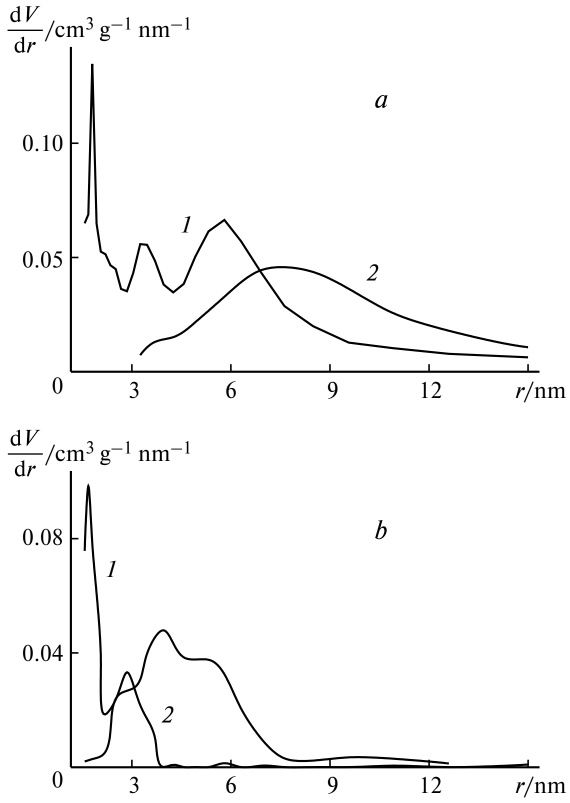


Fig. 2. Curves of pore volume size distribution (*V*) on catalysts **1** (*a*) and **2** (*b*) before (*1*) and after (*2*) calcination at 700 °C.

The reaction between H_2S and *n*-pentane was carried out at 550 °C, flow rate $\upsilon = 0.6$—$0.8\ h^{-1}$, and feed ratios $H_2S : n\text{-}C_5H_{12} = 2$—$3$ and $n\text{-}C_5H_{12} : N_2 = 0.6$—$1.6$. The reaction of H_2S with piperilene was carried out at 500 °C and $\upsilon = 0.3$—$0.4\ h^{-1}$. The results obtained are presented in Table 2.

Table 2. Heterocyclizion properties of the chromium oxide catalysts in the reactions of piperilene and *n*-pentane with H_2S

Initial hydrocarbon	Catalyst	Yield of liquid catalyst (wt.%)	Composition of liquid catalyst (wt.%)					Yield of 2-methylthiophene (wt.%)	
			Initial hydrocarbon	Other products C_5	Thiophene	2-Methylthiophene	3-Methylthiophene	I[a]	II[b]
Piperilene	**1**	100	8.1	8.0	9.0	71.4	3.5	71.4	77.7
	2	100	5.0	17.7	5.3	69.2	2.8	69.2	72.8
n-Pentane	**1**	87.1	39.8	7.6	7.2	43.2	2.2	37.6	57.6
	2	86.1	44.9	8.3	7.4	36.4	3.0	31.3	51.0

[a] Calculated per hydrocarbon passed.

[b] Calculated per reacted hydrocarbon.

Results and Discussion

The initial catalyst **1** dried at 120 °C and evacuated at 400 °C has the specific surface $S_{sp} = 160$ m^2 g^{-1} and total pore volume $V = 0.43$ cm^3 g^{-1} (see Table 1). The porous structure of this catalyst is substantially nonuniform and contains pores with the size r ranging from 1.8 to 7 nm. Three peaks at 1.8, 3.3, and 5.7 nm are seen in the curve of pore volume size distribution (see Fig. 2, *a*). After calcination at 700 °C, the specific surface of the catalyst is almost halved (86 m^2 g^{-1}), while the total pore volume remains unchanged. The pore size increases, the narrow pores with $r = 1.8$—3.0 nm disappear completely, a broad maximum at $r = 7.5$ nm is observed in the pore size distribution curve, and the contribution of large pores with $r > 9$ nm increases.

Noncalcined catalyst **2** has almost the same specific surface (155 m^2 g^{-1}) as catalyst **1**. After calcination at 700 °C the specific surface of the catalyst containing α-Al_2O_3 and boehmite is also halved (to 74 m^2 g^{-1}), and the total pore volume also remains essentially unaffected but it is nearly twice as small in absolute value as for catalyst **1**. The curve of pore size distribution for the noncalcined catalyst (see Fig. 2, *b*) contains only two maxima at 1.7 and 2.8 nm. Fine pores of both catalysts have the same size, whereas unheated catalyst **2** contains almost no large pores. After the calcination of catalyst **2** the narrow pores with $r = 1.7$ nm disappear as in sample **1** but some pores with $r = 2.7$ nm are retained and, in addition, larger pores with size of 3.5—7.0 nm appear. The maximum in the pore size distribution curve corresponds to ~4.0 nm, and pores with $r > 7.0$ nm are virtually absent.

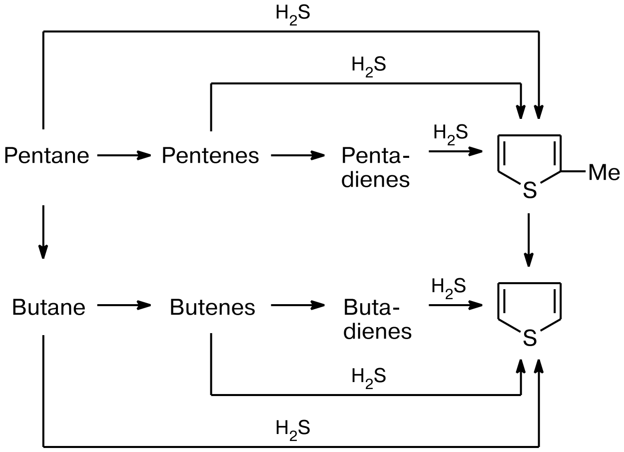
Thus, the textures of the Cr_2O_3-K_2O/Al_2O_3 catalysts containing REE oxides and having the same chemical composition but different modifications of the oxide support differ. Sample **1** containing only γ-Al_2O_3, unlike sample **2** additionally containing α-Al_2O_3 and AlOOH, is characterized by a greater pore volume and larger pores in both the uncalcined and calcined catalysts.

2-Methylthiophene is the main product of the reaction of H_2S with piperilene or *n*-pentane on the catalysts under study.

On both catalysts piperilene produces 2-methylthiophene in amount approximately twice as that *n*-pentane does. The yield of 2-methylthiophene in the reaction of H_2S with *n*-pentane on the γ-Al_2O_3-based catalyst (**1**) is somewhat higher than that on the α-Al_2O_3-containing catalyst (**2**). In both cases, piperilene produces almost the same amount of the product (71.4 and 69.2%, respectively).

The mechanism of formation of 2-methylthiophene on the catalyst containing chromium, lanthanum, potassium, and aluminum oxides has previously[9,10] been studied by the isotope-kinetic methods using ^{14}C atoms. The measurement of the concentration and molar radioactivity of the products formed from *n*-pentane with a minor addition of labeled molecules made it possible to find the rates of particular stages, determine the reactions involving both pentane and pentene, and propose the mechanism of the process (Scheme 1).

Scheme 1



2-Methylthiophene is formed from H_2S and *n*-pentane predominantly *via* consecutive reactions including intermediate dehydrogenation to pentenes and pentadienes. The dehydrogenation products, *viz.*, butenes and butadiene, are involved in the formation of thiophene molecules. An insignificant portion of 2-methylthiophene is the product of direct interaction of *n*-pentane with H_2S, and thiophene is partially formed by the interaction of H_2S with *n*-butane or butene and by the demethylation of 2-methylthiophene.

According to the mechanism proposed (see Scheme 1), the heterocyclization of *n*-pentane on the Cr_2O_3-K_2O/Al_2O_3 catalyst containing lanthanum oxide should occur mainly through dehydrogenation. Perhaps, the large pores of 6—10 nm in the γ-Al_2O_3-based catalyst favors the enhancement of the dehydrogenating properties. Comparing catalysts **1** and **2** a lower dehydrogenating activity of catalyst **2** is related, most likely, to the α-Al_2O_3 modification and boehmite in the composition of its support.

If 2-methylthiophene is obtained by the reaction of H_2S with piperilene, according to the mechanism presented above, dehydrogenation is not necessary. This is confirmed by the results of experiments with catalyst **2** that differs from catalyst **1** in having finer pores and a smaller total pore volume: the yield of 2-methylthiophene on catalysts **1** and **2** is virtually the same.

Thus, the sample containing γ-Al_2O_3 is a more efficient catalyst for the synthesis of 2-methylthiophene by the reaction of *n*-pentane with H_2S. In the reaction of piperilene with H_2S both catalysts, which have the same chemical composition but differ in modification of the support (alumina), exhibit the same efficiency.

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