Chemistry of Heterocyclic Compounds, Vol. 46, No. 9, 2010

INVESTIGATION OF THE MECHANISM OF CATALYTIC RECYCLIZATION OF FURAN TO THIOPHENE

A. V. Mashkina[1]*

Investigation of the formation of thiophene from furan and hydrogen sulfide at various catalysts showed that the activity of the catalysts increases with increase in the strength and concentration of Lewis acid centers. It was found by IR spectroscopy that if the degree of coverage of the aluminum oxide surface with hydrogen sulfide is higher than monolayer its dissociative chemisorption does not occur. Mechanism was postulated wich assume that the reaction takes place through stage with the formation of a surface intermediate, including coordination of the α-carbon atoms of the furan ring with the Lewis acid center and with the sulfur atom of molecular hydrogen sulfide.

Keywords: hydrogen sulfide, thiophene, furan, catalysts, adsorption.

The catalytic recyclization of furan in an H_2S medium discovered by Yur'ev [1] forms the basis of the production of thiophene [2-4]. It was assumed that the transformation of the furan ring into a thiophene ring takes place according to the following scheme: Interaction of the furan with the surface of the catalyst leads to cleavage of the furan ring at the C–O bond; the H_2S adds to the released bonds, and an unsaturated hydroxymercapto compound, which is dehydrated by the action of the catalyst and closes to a thiophene ring, is formed. The decomposition of the furan during the reaction was judged from the obtained side products – hydrocarbons and carbon monoxide.

In the author's opinion indirect evidence for the scheme was provided by the fact that the saturated hydroxymercapto compound is easily hydrated to tetrahydrothiophene by the action of aluminum oxide [1]. The scheme was also adopted in later papers [5-7] on study of the catalytic reaction of furan with H_2S. The presence of the side products and the surface carbonate and carbonate-like structures and O–C=O and –CH_2– fragments, detected in the IR spectra of the adsorbed furan, was presented as evidence fact that the reaction takes place through decomposition of the furan ring at the Na and Li forms of NaX and NaY zeolites and at V and Mo oxides. According to [5], the reaction at alkaline zeolites involves participation of the acceptor centers of the catalyst since the process is facilitated with increase in the density and polarizing action of the cations. In the opinion of the authors of [7] the participation of Al^{3+} cations in the recyclization of furan at Al_2O_3 is demonstrated by the fact that both the strength and the concentration of the Lewis acid centers (*L*-centers) and the activity of the catalyst decrease when the preliminary calcination temperature of the Al_2O_3 is increased above 550°C.

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* To whom correspondence should be addressed, e-mail: bic@catalysis.ru.

[1] G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Novosibirsk 630090, Russia.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1320-1325, September, 2010. Original article submitted October 14, 2009.

0009-3122/10/4609-1063

It was assumed [5-7] that the recyclization of furan to thiophene takes place through a stage involving the formation of a bond between the acceptor center of the catalyst and the oxygen atom of the furan, while the α-carbon atoms of the ring bond with the surface oxygen. The authors of [7] suggest that H_2S dissociatively chemisorbed on the acid–base centers of the Al_2O_3 surface takes part in the recyclization of the furan ring to thiophene, but this was not verified experimentally. In the present work a conclusion about a mechanism of catalytic recyclization of furan in the H_2S medium was reached on the basis of an investigation into the reaction in the presence of catalysts differing in Lewis acidity and of data on the adsorption of H_2S.

The experiments showed that at 250-450°C γ-Al_2O_3 exhibits high activity in the reaction of furan with H_2S leading to the formation of thiophene (Table 1). As seen, at constant temperature, with constant reagent concentrations, and a constant molar ratio of H_2S to furan (M) the degree of conversion of the furan (X, %) and the yield of thiophene (y, mol %) increase with increase in the reaction time; the reaction rate increases with increase in temperature. Under certain conditions the yield of thiophene amounts to ~100%; the side products (CO and ethylene) are formed with yields of 0.3-4.0 mol %; the selectivity of the formation of thiophene is close to 100%. With a contact time significantly longer than the time required for the attainment of X = 100% an increase in the yield of the side products and, accordingly, a decrease in the yield of thiophene are observed. The low yield of thiophene (y = 31-37%) and the formation of a large amount of side products at Al_2O_3 observed in the papers by Yur'ev are probably due to realization of the reaction with a very long contact time.

Experiments on the recyclization of furan at γ-Al_2O_3 at 400°C with $M \approx 7.0$ showed that the yield of thiophene is not affected by change in the initial concentration of furan (c_0, mmol/l).

c_0, mmol/l	0.7	1.0	1.7	2.6	3.3
y, mol. %	72	70	74	71	73

This indicates that the recyclization of furan to thiophene is of first order.

In order to compare the activity of the catalysts experiments were conducted at γ-Al_2O_3 at 400°C with c_0 = 0.6-0.7 mmol/l, M = 8.0-7.2, and X = 30-90%. The activity of the various catalysts was characterized by the first-order rate constant (k, sec^{-1}) (Table 2).

On the surface of the employed catalysts strong protic centers, basic centers (BC) of moderate strength with deuterium affinity to surface oxygen (PA^o) = 800-900 kJ/mol, and L-centers of various strengths and

TABLE 1. Dependence of the Transformation of Furan in Hydrogen Sulfide in the Presence of γ-Al_2O_3 on Temperature and on the Contact Time (c_0 = 0.6-0.7 mmol/l, M = 6.8-7.2)*

τ, sec	X, %	S, %	τ, sec	X, %	S, %
	T 250°C			T 400°C	
7.4	30	100	1.2	52	100
11.7	52	98	1.7	77	99
14.0	63	95	2.3	98	99
	T 300°C			T 420°C	
2.5	40	99	1.0	56	98
3.6	56	98	1.7	89	99
5.5	91	97	2.1	98	98
	T 350°C			T 450°C	
2.4	53	98	1.0	56	99
4.0	86	99	1.5	82	99
4.6	94	96	1.8	95	96

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*τ is the contact time, S is the selectivity of formation of thiophene.

TABLE 2. The Activity of the Catalysts in the Recyclization of Furan to Thiophene (T 400°C, c_0 = 0.6-0.7 mmol/l, M = 6.8-7.2)

Catalyst	Q_{CO}, kJ/mol	c_L, μmol/g	k, sec^{-1}	S, %
MoO_3/SiO_2	27	150	0.04	69
Cr_2O_3/SiO_2	28	340	0.06	74
WO_3/SiO_2	29	220	0.08	81
NaX	20	2400	0.15	88
$MoO_3/\gamma\text{-}Al_2O_3$	35	280	0.22	96
$Cr_2O_3/\gamma\text{-}Al_2O_3$	36	500	0.32	99
$WO_3/\gamma\text{-}Al_2O_3$	37	380	0.45	98
$\gamma\text{-}Al_2O_3$	34–36	470	0.85	99
	40–55.5	142		

concentrations were practically absent. It is seen from the data in Table 2 that the reaction of furan with H_2S takes place at a low rate in the presence of Cr, Mo, and W oxides deposited on SiO_2 and on zeolite NaX, having very weak *L*-centers, even at high concentrations, and S = 74-88%. An increase of rate and the attainment of an S value of up to 100% are observed when the reaction is conducted in the presence of aluminum oxide catalysts.

Among the investigated catalysts the highest activity is exhibited by $\gamma\text{-}Al_2O_3$, which has a large content of strong *L*-centers. The obtained result demonstrates the importance of the *L*-centers in the formation of thiophene from furan and H_2S.

The absorption bands from the "basic" (ν = 3780-3750) and "acidic" (ν = 3600 cm^{-1}) OH groups on the surface of inicial $\gamma\text{-}Al_2O_3$ were determined from the IR spectra. There are basic centers (BC) of moderate strength with c_{BC} = 1110 μmol/g and strong *L*-centers due to the presence of a significant concentration of Al^{3+} cations (c_L = 612 μmol/g) (with heat of adsorption of CO Q_{CO} = 34-56 kJ/mol).

In the IR spectrum of the gaseous H_2S there are absorption bands from the stretching vibrations of the SH groups (ν = 2611, 2682) and the deformation vibrations of the H–SH groups (ν = 1290 cm^{-1}). After the admission of gaseous H_2S to the catalyst sample at room temperature at the rate of 0.6 mmol calculated on 1 g of catalyst (which is approximately equal to the concentration of the *L*-centers of $\gamma\text{-}Al_2O_3$) the absorption bands of H_2S in the IR spectrum are shifted to ν = 2570 and ν = 1334 cm^{-1} respectively. Changes are also observed in the IR spectrum of the OH groups of the catalyst: The absorption bands of the OH groups of "basic" character disappear, and the intensity of the absorption bands at ~3550 cm^{-1} (the vibrations of the "acidic" OH groups) increases. After vacuum treatment of the sample with adsorbed H_2S at room temperature it was found that c_L = 122 and c_{BC} = 278 μmol/l, i.e., a large part of the *L*-centers and basic centers are blocked (by 75-80%) during the adsorption of H_2S. The admission of gaseous H_2S at the rate of 3.2 mmol/g (approximately monolayer surface coverage) leads to some increase in the intensity of the absorption bands belonging to the surface SH and OH groups. After vacuum treatment of the sample at 200°C a large part of the *L*- and basic centers are freed, and the concentration of the centers increases (c_L = 475, c_{BC} = 820 μmol/g); the intensity of the absorption bands in the region of the vibrations of the "acidic" OH groups increases, and absorption bands from the "basic" OH groups appear. The symbate removal of the SH absorption bands and the change in the intensity of the OH absorption bands during thermal desorption indicate dissociative chemisorption of the H_2S on the $\gamma\text{-}Al_2O_3$ involving the *L*-centers and the basic centers of the catalyst with the cleavage of one H–S bond and the formation of OH and SH groups; cleavage of both H–S bonds with the release of sulfur probably also occurs to a small degree. With further increase in the amount of gaseous H_2S admitted to the sample (up to 5.2-8.0 mmol/g) no appreciable changes are observed in the concentration of the acid–base centers of the catalyst or in the IR spectrum of the adsorbed H_2S, i.e., a large part of the H_2S remains in the undecomposed form.

Most of the experiments on the recyclization of furan to thiophene at γ-Al_2O_3 were conducted with a large excess of H_2S in relation to the furan. Here the amount of H_2S in millimoles calculated for 1 g of catalyst was 1-2 orders of magnitude greater than that required for monolayer coverage of the surface. Moreover, it follows from the catalytic experiment that the activity of the catalyst increases with increase of *M*. At 400°C, for example, the following results were obtained:

M	0.4	2.8	4.1	7.0	11	18	20
k, sec^{-1}	0.03	0.24	0.40	1.0	1.15	1.94	2.3

These data can serve as a further argument in favour of the conclusion that the recyclization of furan to thiophene takes place with the participation of molecular H_2S.

It thus follows from the experiments that the *L*-centers play an important role in the activity of the catalysts for the recyclization of furan to thiophene and that molecular H_2S participates in the process.

The surface fragments of decomposed furan detected in the IR spectra and the presence of the reaction side products probably result from prolonged interaction of the substrate with the catalyst. As shown by our experiments on the transformation of furan in the absence of H_2S at γ-Al_2O_3 at 400°C with $\tau = 1.5\text{-}4.2$ sec the furan undergoes insignificant decomposition with a yield of 1-5 mol % of side products.

The idea that a bond is formed between the *L*-center of the catalyst and the oxygen atom of the furan ring during contact between the furan and the catalyst is unfounded. From quantum-chemical calculations [6] and from some experimental data [8, 9] it follows that the furan is adsorbed flatly on the catalysts and not perpendicularly as required during coordination involving the oxygen of the ring. On account of the participation of electrons from the furan oxygen atom in aromatic conjugation it is depleted in electrons and loses significant ability for complex formation with the acceptor centers. At the same time as a result of aromatic conjugation the α-carbon atoms of the furan are enriched in electrons, and this must facilitate their interaction with the acceptor centers of the catalyst. Recyclization of the furan without its previous decomposition at the C–O bond therefore seems more likely. During contact between the furan and γ-Al_2O_3 a surface complex involving the formation of a bond between the α-carbon atoms of the furan ring and the *L*-centers of the carbon and the sulfur atom of molecular hydrogen sulfide is formed. Thiophene is released during the dehydration of this surface intermediate.

EXPERIMENTAL*

"Pure" and "chemical-purity" reagents were employed. The hydrogen sulfide (99.5% purity) was obtained by the catalytic reaction of H_2 and S. The catalyst and support was γ-Al_2O_3 ($S_{sp} = 275$ m^2/g), prepared by heat treatment of pseudoboehmite aluminum hydroxide; a ready-made sample of silicon dioxide was also used as support (SiO_2, $S_{sp} = 330$ m^2/g). The zeolite NaX was a ready-made sample. The deposited catalysts were prepared by impregnation of the support up to its moisture-retaining capacity with aqueous solutions of ammonium tungstate, ammonium molybdate, and chromium nitrate. The samples were dried in air at room temperature for 12 h and at 110°C for 5 h and calcined at 500°C in a stream of dry air for 5 h. Composition of catalyst, wt. %: 5 Cr_2O_3 on SiO_2 and Al_2O_3; 10 MoO_3 and WO_3 on SiO_2; WO_3/Al_2O_3; 15 MoO_3/Al_2O_3.

The IR spectra were recorded on a Specord 751 R spectrometer. The acid–base characteristics of the catalysts were determined by IR spectroscopy from the adsorption of CO and $CDCl_3$ by the known procedure [10]. The following were introduced into the cuvette: CO at 100-120 K ($p_{CO} = 30$ mm Hg); liquid $CDCl_3$ at 250 K, 1-5 μl. The strength of the centers in kJ/mol was estimated as follows: *L*-centers from the heat of

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*L. N. Khairulina and I. V. Desyatov took part in the work.

adsorption of CO; basic centers from the affinity of the deuterium of the $CDCl_3$ to the basic centers (PA°). The concentration of the centers is given in μmol calculated for 1 g of catalyst.

The adsorption of H_2S on γ-Al_2O_3 was investigated by IR spectroscopy. The catalyst sample was compressed into a tablet with a "thickness" of 10-15 mg/cm^2 and was baked under vacuum at 400°C for 2 h. Hydrogen sulfide was delivered to the sample at room temperature, and the IR spectrum was recorded. The sample was then treated under vacuum without heat or at 200°C for 2 h, after which the strength and concentration of the basic centers and *L*-centers were determined.

The experiments on the recyclization of furan to thiophene were conducted at atmospheric pressure in flow-type apparatus on a stationary layer of catalyst measuring 0.25-0.50 mm under conditions with the absence of diffusion complications. Helium was delivered to the cooled saturator filled with furan and, after mixing with H_2S, to the reaction vessel. The initial mixture and the reaction products were analyzed on an LKhM-8MD chromatograph with a katharometer (2 m×3 mm column, Porapak Q + R 1:1). The contact time is equal to the ratio of the volume of the catalyst (cm^3) to the gas flow rate (cm^3/sec) at atmospheric pressure and room temperature. The conversion of furan, the yields of the products, and the selectivity with respect to thiophene (equal to the ratio of the yield of thiophene to the conversion of furan) were calculated.

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