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Catalytic Reactions of *n*-Propanol and *n*-Butanol with Hydrogen Sulfide

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Abstract—The transformations of *n*-propanol and *n*-butanol in an H_2S atmosphere at T = 300–350°C and P = 0.1 MPa in the presence of acid–base catalysts were studied. Only alcohol dehydration with the release of alkenes occurred at a high rate on catalysts with strong proton sites (tungstosilicic and tungstophosphoric acids on SiO_2 or a decationized high-silica zeolite), whereas alcohol thiolation with the formation of alkanethiols also occurred on catalysts with Lewis acid sites (Al_2O_3; NaX; MgO; Cr/SiO_2; and Al_2O_3 modified with W, K, Na, K_2WO_4, or Na_2WO_4). The rate of reaction decreased with decreasing strength of Lewis acid sites and with increasing strength of basic sites; however, the selectivity of thiol formation increased. Alumina modified with alkaline additives was the most selective catalyst. In the presence of this catalyst, an alcohol selectively reacted with H_2S to form an alkanethiol, and the alkanethiol underwent partial decomposition with the release of an alkene and H_2S at a long contact time.

INTRODUCTION

The interaction of H_2S with aliphatic alcohols in the presence of solid catalysts can result in the formation of alkanethiols and dialkyl sulfides—important sulfur-containing compounds. The reaction of H_2S with methanol was studied in most detail (see the review [1]). Data on the thiolation of its homologues, in particular, normal propanol and butanol, are much more scanty. In the reaction of propanol at atmospheric pressure in an excess of H_2S at T = 250–350°C, the yield of propanethiol was 1–3 mol % on HNaY and NTsVK zeolites [2], HPW heteropoly acid [3], Al_2O_3 [4], and WO_3/Al_2O_3 [5]; this yield was as high as ~20 mol % on NaX and CdNaX zeolites [2, 3] or up to 80 mol % on K_2WO_4/Al_2O_3 [6]. Dipropyl sulfide with a yield lower that 10 mol % was formed in the reaction of propanol with H_2S on CdNaX zeolite at T = 350°C [7]. At T = 300°C and complete conversion of butanol on Al_2O_3 and NaX catalysts, *n*-butanethiol was formed in a 35 mol % yield [8], whereas the yield was 50 mol % on ThO_2 supported on pumice at T = 260–380°C [9]. The catalysts were not compared quantitatively in terms of activity and selectivity in the thiolation of propanol and butanol.

In this work, we studied the reactions of propanol and butanol in an H_2S atmosphere in the presence of various acid–base catalysts.

EXPERIMENTAL

Stock-produced samples of SiO_2 (KSK brand; S_{sp} = 305 m^2/g), γ-Al_2O_3 (A-1 brand; S_{sp} = 200 m^2/g), MgO (S_{sp} = 17 m^2/g), zeolite NaX (S_{sp} = 800 m^2/g), and high-silica zeolite HZSM-5 (S_{sp} = 500 m^2/g) were used as catalysts. Supported catalysts were prepared by the incipient wetness impregnation of SiO_2 and Al_2O_3 with the use of aqueous solutions of tungstophosphoric (HPW) and tungstosilicic (HSiW) acids; ammonium, potassium, or sodium tungstate; chromium nitrate; sodium hydroxide; and potassium carbonate. The prepared samples were dried in air at T = 110°C for 5 h and calcined in a flow of air for 3 h (NaX, K_2WO_4/Al_2O_3, and Na_2WO_4/Al_2O_3 were calcined at T = 400°C; the other samples, at T = 500°C; and supported heteropoly acids were calcined at T = 300°C in a helium flow). The concentrations of active substances in the catalysts were the following (wt %): 25, HPW/SiO_2, $HSiW/SiO_2$, and K_2WO_4/SiO_2; 15, Na_2WO_4/Al_2O_3 and K_2WO_4/Al_2O_3; 24, W/Al_2O_3; 1.5, Cr/SiO_2; 3.6, K/Al_2O_3 and K/SiO_2; and 0.01–3.0, Na/Al_2O_3. Before activity measurements, the samples were treated with a mixture of 25% H_2S + 75% He for 1 h. Data on the acid–base properties of the catalysts used were obtained previously and published elsewhere [1, 10, 11]. They were determined [10] by IR spectroscopy from the adsorption of pyridine, CO, or $CDCl_3$. In this case, the site strength (in kJ/mol) was estimated from the proton affinity to pyridine (PA^a) for proton sites, from the proton affinity of $CDCl_3$ to a basic site (PA^b) for basic sites, or from the heat of CO adsorption (Q_{CO}) for Lewis acid sites (L-sites). Reagent-grade and chemically pure chemicals were used in this study. Hydrogen sulfide (99.5% purity) was prepared by the reaction of H_2 with S on an AlNiMo catalyst.

The experiments were performed in a circulation flow setup at atmospheric pressure. Helium from a gas cylinder was supplied to a thermostated saturator filled with propanol or butanol. Helium saturated with an alcohol was mixed with helium-diluted H_2S, which was supplied from another gas cylinder. Next, the mixture

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was directed to a reactor filled with a catalyst; the reactor was heated using an immediate-action furnace. The reaction mixture was agitated using a circulation pump at a circulation rate of 400 l/h, which was sufficient to equalize concentrations before and after a catalyst bed. The entire system was thermostated at $T = 160 \pm 10°C$. The initial substances and reaction products were sampled for analysis at regular intervals. The analysis was performed on an LKhM-8MD chromatograph with a thermal-conductivity detector (a column (2 m × 3 mm) packed with Porapak Q and Porapak R (1 : 1); helium was the carrier gas). The experiments were performed using catalysts with a particle size of 0.25–0.5 mm in the absence of diffusion limitations. Fresh catalyst portions were used in every experiment. The duration of an experiment was 1 h. The ratio of the catalyst volume (cm^3) to the gas flow rate (cm^3/s) at 20°C and $P = 0.1$ MPa was taken as the contact time (τ, s). Based on the results of analysis, the alcohol conversion (X, %), the yields of products (Y, mol %), the selectivity ($S = Y/X$, %), and the rates of overall alcohol conversion and product formation per gram of catalyst (w, mmol h^{-1} (g Cat)$^{-1}$) or per L-site (w_L, μmol/h) were calculated.

RESULTS AND DISCUSSION

Previously, we found that propanol and butanol were not converted without a catalyst at $T = 300–350°C$ and initial alcohol and H_2S concentrations of 3.5 and 14 vol %, respectively. The addition of a catalyst was favorable for the occurrence of a reaction, and the reaction path depended on catalyst composition. For example, the catalytic process on Al_2O_3 in an atmosphere of H_2S occurred more rapidly than that in the absence of H_2S (Fig. 1). The experiments on the conversion of propanol and butanol were performed at $T = 300°C$ in a large excess of H_2S over an alcohol: $M = (10–14) : 1$ (M is the molar ratio of H_2S to an alcohol) at various contact times. Tables 1 and 2 summarize some results.

The reaction of propanol on the HPW/SiO_2 catalyst began at $\tau < 0.01$ s; an increase in the contact time resulted in an increase in the conversion of propanol, and propanol was completely decomposed at $\tau = 0.2$ s. The conversion of butanol on the HZSM-5 and $HSiW/SiO_2$ catalysts began at $\tau < 0.003$ and 0.04 s, respectively, and it was completely decomposed at $\tau = 0.045$ and 0.3 s, respectively. In the range $X = 20–100\%$, an alkene (propylene from propanol or 1-butylene and a minor amount of 2-butylene from butanol) was the only product on the above catalysts. In this case, the alkene yield was equal to the alcohol conversion, and sulfur-containing compounds were not formed; that is, on these catalysts, only the following reactions of alcohol dehydration occurred:

$$C_3H_7OH = C_3H_6 + H_2O, \quad \text{(I)}$$

$$C_4H_9OH = C_4H_8 + H_2O. \quad \text{(II)}$$

Alkenes did not undergo further transformations, in particular, with the participation of H_2S, on the specified catalysts. Thus, the selectivity of alkene formation was equal to 100% if the reaction was performed in an H_2S atmosphere at a contact time much longer than that required for attaining $X = 100\%$ ($\tau = 0.5$ s for propanol, and $\tau = 1–5$ s for butanol). It is well known [11] that alkanethiols and dialkyl sulfides are readily decomposed on acid catalysts with the elimination of H_2S and an alkene; it is likely that this fact can explain the absence of sulfur-containing compounds among the reaction products.

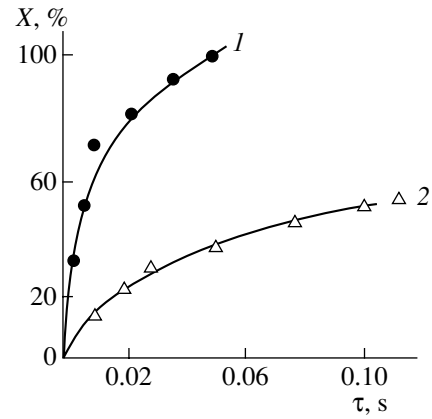

Fig. 1. Effect of contact time on propanol conversion in the presence of γ-Al_2O_3 at $T = 300°C$ and molar ratios between H_2S and propanol of (*1*) 14 and (*2*) 0.

Dipropyl ether was formed on the NaX, Al_2O_3, and 0.5% Na/Al_2O_3 catalysts as a result of propanol conversion. The yield of this ether decreased with contact time, and the selectivity decreased with propanol conversion, probably because of the occurrence of the reaction

$$(C_3H_7)_2O \longrightarrow C_3H_6 + C_3H_7OH$$
$$\hookrightarrow 2C_3H_6 + H_2O. \quad \text{(III)}$$

On the other tested catalysts, the conversion of propanol or butanol took place without the step of ether formation or ether dehydration occurred at a very high rate; therefore, ethers were not detected among the reaction products.

In the presence of catalysts with Lewis acid sites (NaX, Cr/SiO_2, Al_2O_3, MgO, W/Al_2O_3, Na/Al_2O_3, and K/Al_2O_3) in an H_2S atmosphere, the alcohols underwent not only dehydration but also thiolation with the formation of propanethiol and *n*-butanethiol. The presence of 2-propanethiol or 2-butanethiol was detected in none of the cases, and dialkyl sulfides were not formed. However, it is likely that a dialkyl sulfide was formed at the initial stage; however, it was rapidly decomposed. It is well known [11] that the catalytic decomposition of dialkyl sulfides occurs at a much higher rate than that of alkanethiols. This assumption is based on our finding that the rate of alcohol conversion in an H_2S atmosphere is higher than the rate of conversion in helium

Table 1. Effect of contact time on the catalytic conversion of *n*-propanol in an H_2S atmosphere at T = 300°C, $[propanol]_0$ = 3.5–3.0 vol %, and $[H_2S]_0$ = 46–48 vol %

Catalyst*	τ, s	*X*, %	*Y*, mol %			*S*, %		
			C_3H_7SH	C_3H_6	$(C_3H_7)_2O$	C_3H_7SH	C_3H_6	$(C_3H_7)_2O$
HPW/SiO_2	0.036	30	0	30	0	0	100	0
	0.090	72	0	72	0	0	100	0
NaX	0.009	24	10	11	3	42	46	12
	0.110	80	32	46	1	40	57	1
W/Al_2O_3	0.009	44	16	27	0	36	62	0
	0.036	75	28	45	0	37	60	0
γ-Al_2O_3	0.00324	34	15	14	4	44	41	12
	0.036	93	42	44	2	45	47	2
Na_2WO_4/Al_2O_3	2.0	21	18	3	0	86	14	0
	9.0	80	69	10	0	86	12	0
$0.3Na/Al_2O_3$	0.18	16	10	4	2	63	25	12
	1.08	78	53	20	4.7	68	26	6
$1.7Na/Al_2O_3$	1.1	30	29	1.5	0	97	5	0
	6.8	89	87	2.2	0	98	2	0
$2.1Na/Al_2O_3$	1.7	46	44	3	0	95	5	0
	6.8	75	70	5	0	93	7	0

* Figures before Na indicate its concentration in the catalyst in wt %.

Table 2. Effect of contact time on the catalytic conversion of *n*-butanol in an H_2S atmosphere at T = 300°C, $[butanol]_0$ = 1.3–1.4 vol %, and $[H_2S]_0$ = 13–14 vol %

Catalyst	τ, s	*X*, %	*Y*, mol %		*S*, %	
			C_4H_9SH	C_4H_8	C_4H_9SH	C_4H_8
$HSiW/SiO_2$	0.04	38	0	37	0	97
	0.18	92	0	90	0	98
HZSM-5	0.003	26	0	26	0	100
	0.025	90	0	89	0	99
NaX	0.34	27	11	15	41	56
	2.12	83	35	50	42	60
W/Al_2O_3	0.02	36	13	22	37	62
	0.09	88	29	57	33	65
Cr/SiO_2	0.90	37	7	28	19	76
	7.90	92	21	72	23	78
γ-Al_2O_3	0.01	39	13	25	34	64
	0.05	90	32	56	36	62
K/Al_2O_3	1.73	45	44	1	97	3
	8.60	92	90	1.8	98	2

(for example, see Fig. 1). The selectivity of thiol formation on Al_2O_3, W/Al_2O_3, NaX, and Cr/SiO_2 catalysts was no higher than 20–50%. With increasing contact time on these catalysts, the alcohol conversion and the yields of alkenes and thiols increased (Fig. 2), whereas the selectivity remained unchanged as the alcohol conversion increased up to at least X = 80% (Tables 1, 2, and Fig. 3). That is, these products were independently formed from alcohols:

$$\begin{aligned} ROH &\xrightarrow{-H_2S} RSH + H_2O \\ &\hookrightarrow R'CH = CH_2 + H_2O, \end{aligned} \qquad \text{(IV)}$$

where R is Pr or Bu; R' is Me or Et.

We found that under the test conditions the resulting alkenes did not react with H_2S. Thus, the formation of propanethiol on Al_2O_3 was not observed at T = 75–360°C, H_2S : propylene = (2–22) : 1, τ = 0.2–166 s, and a propylene conversion of 1–100%. In some cases, 2-propanethiol was detected in trace amounts.

In the presence of alkali-modified Al_2O_3, the selectivity of thiol formation was 70–99% depending on the alkali content. It changed with experimental conditions. At a long contact time, the release of H_2S and an olefin because of alkanethiol decomposition was also observed on these catalysts. For example, on the K/Al_2O_3 catalyst at T = 300°C, the conversion of butanol increased with contact time; the selectivity of *n*-butanethiol formation remained constant over a considerable range of alcohol conversions; it somewhat decreased at a high conversion; and the selectivity of butylene formation increased (Fig. 4). The conversion of butanol decreased with the H_2S-to-butanol ratio; however, in this case, the selectivity of *n*-butanethiol formation increased (Fig. 5). At T = 300°C and M = 10, the selectivity of *n*-butanethiol formation was 100% at a butanol conversion of 20%, whereas it decreased to 90% at X = 100%. The selectivity decreased with temperature: at T = –330°C and X = 20 and 100%, the selectivity of *n*-butanethiol formation was 99 and 84%, respectively, whereas S = 85 and 51%, respectively, at T = 350°C.

On all of the catalysts tested, the rate of butanol conversion in an H_2S atmosphere was lower than that of propanol conversion. However, the activity and selectivity as functions of catalyst composition exhibited the same behaviors. The activity and selectivity of catalysts in the reactions of propanol and butanol conversion in an H_2S atmosphere were affected by the acid–base properties of catalyst surfaces. The alcohols were converted at a low rate on silica gel, which has weak proton sites (PA^a = 1390 kJ/mol) and weak basic sites (PA^b < 800 kJ/mol). The rate of conversion significantly increased in the case of HPW/SiO_2, $HSiW/SiO_2$, and HZSM-5 catalysts containing strong proton sites (PA^a < 1180 kJ/mol) and weak basic sites. It is likely that the enhanced activity of zeolite HZSM-5 in the conversion of butanol was due to the presence of a small amount of very strong L-sites, which also participated in the reaction, on its surface. In the presence of all of the above proton-donor catalysts, alcohol thiolation did not occur, and sulfur-containing compounds were absent from the reaction products. The surfaces of

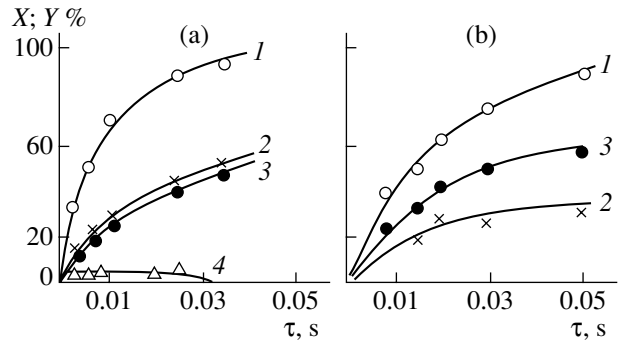

Fig. 2. (*1*) Alcohol conversion and the yields of (*2*) thiols, (*3*) alkenes, and (*4*) dipropyl ether on γ-Al_2O_3 at T = 300°C as functions of contact time. (a) The reaction of propanol (M = 14) and (b) the reaction of butanol (M = 10; M is the H_2S-to-alcohol molar ratio).

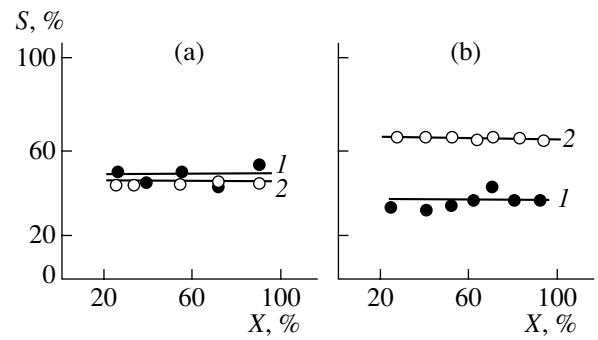

Fig. 3. Selectivities of (*1*) thiol and (*2*) alkene formation on γ-Al_2O_3 at T = 300°C at different conversions of (a) propanol and (b) butanol; M = 14 (propanol) and M = 10 (butanol).

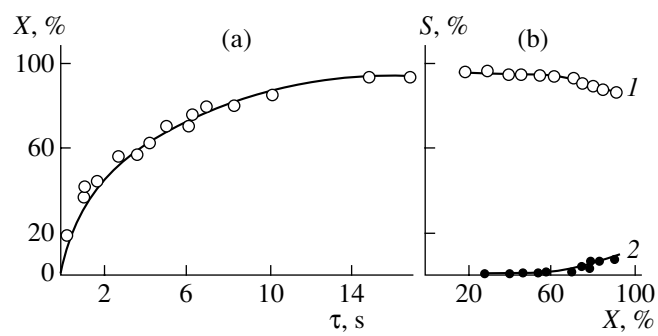

Fig. 4. (a) Effect of contact time on butanol conversion and (b) the selectivities of (*1*) butanethiol and (*2*) butylene formation as functions of butanol conversion. K/Al_2O_3 catalyst; T = 300°C; M = 10.

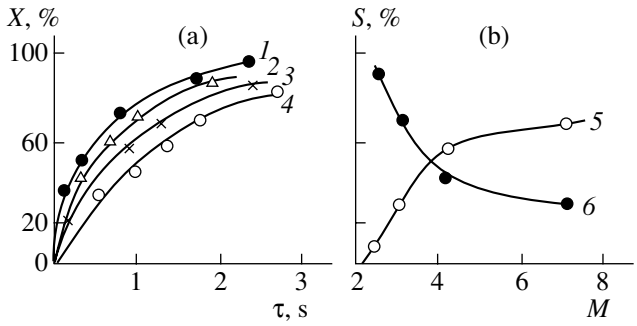

Fig. 5. (a) Butanol conversion at $T = 350°C$ on the K/Al_2O_3 catalyst at $X = 70\%$ and M = (*1*) 1.0, (*2*) 2.2, (*3*) 4.3, and (*4*) 10. (b) Effect of H_2S-to-alcohol molar ratio (M) on the selectivities of (*5*) butanethiol and (*6*) butylene formation.

all of the other tested catalysts contained L-sites (Tables 3, 4) and basic sites. In the presence of these catalysts, the reaction of thiol formation occurred in addition to alcohol dehydration. The NaX, Cr/SiO_2, and MgO catalysts, which have weak Lewis acid sites and basic sites with PA^b = 800–900 kJ/mol on their surfaces, were much less active than Al_2O_3 and W/Al_2O_3, which contain basic sites of the same strength but have stronger L-sites. The addition of potassium or sodium to Al_2O_3 increased the strength of basic sites up to PA^b = 920–950 kJ/mol and decreased the surface acidity. As compared with unmodified Al_2O_3, the rate of alcohol conversion decreased, and the selectivity of thiol formation increased. The higher the alkali content of the catalyst, the greater the increase in the selectivity. The rates of overall conversion of propanol and butanol and of thiol formation per L-site increased with increasing strength of these sites. This fact indicates that these sites are of importance in the reactions of propanol and butanol in an H_2S atmosphere.

It is well known [12–14] that alcohol dehydration occurs under the action of catalyst acid sites, and the rate of dehydration increases with increasing strength of acid sites. It is likely that, because of this, the highest rate of propanol or butanol dehydration was observed on catalysts with strong proton sites (HPW/SiO_2, $HSiW/SiO_2$, and HZSM-5) and strong Lewis sites (Al_2O_3 and W/Al_2O_3). On proton-donor catalysts, an alcohol is activated as a result of the formation of the hydrogen-bonded complex $-M-O-H\cdots\overset{\overset{\displaystyle H}{|}}{O}R$ with a proton site of the catalyst. The decomposition of this complex, either direct or via the step of formation of surface alkoxy structures, results in alcohol dehydration. The alkoxide groups bonded to cations M–OR result from the interaction of an alcohol with L-sites; their subsequent transformation with the participation of basic sites results in alkene elimination. On proton-donor cat-

Table 3. Activity and selectivity of catalysts in the conversion of *n*-propanol at $T = 300°C$, $X = 70\%$, $[propanol]_0 = 3.6$ vol %, and H_2S : propanol = (13–14) : 1

Catalyst*	$w_{propanol}$, mmol h^{-1} (g Cat)$^{-1}$	S, % (to propanethiol)	w_L, μmol/h	
			propanol	propanethiol
SiO_2 (0; 0)	22	0	0	0
$HSiW/SiO_2$ (0; 0)	74	0	0	0
NaX (20; 3.0)	79	20	33.0	6.6
W/Al_2O_3 (36; 1.0)	270	36	1350	486
γ-Al_2O_3 (34; 2.3 and 41; 0.2)**	590	44	1283	564
$0.01Na/Al_2O_3$ (32; 2.4)	581	50	1210	605
$0.3Na/Al_2O_3$ (27; 2.2)	8.0	68	18.0	12.2
$1.7Na/Al_2O_3$ (18; 2.0)	2.0	90	5.0	4.5
$2.1Na/Al_2O_3$ (19; 1.2)	1.4	94	6.0	5.6
$3.0Na/Al_2O_3$ (20; 1.4)	1.0	98	3.6	3.5
K_2WO_4/Al_2O_3 (31; 0.5)	0.60	97	4.8	4.7
Na_2WO_4/Al_2O_3 (32; 1.4)	0.94	96	2.7	2.6

* The heats of CO adsorption (Q_{CO}, kJ/mol), which characterize the strength of L-sites, and their concentrations in μmol/m^2 are given in parentheses. Figures before Na indicate its concentration in the catalyst in wt %.

** Two types of sites.

Table 4. Activity and selectivity of catalysts in the reaction of *n*-butanol in an H_2S at T = 300°C, X = 70%, $[butanol]_0$ = 1.3 vol %, and H_2S : butanol = 10 : 1

Catalyst*	$w_{butanol}$, mmol h^{-1} (g Cat)$^{-1}$	S,% (to butanethiol)	w_L, μmol/h	
			butanol	butanethiol
$HSiW/SiO_2$ (0; 0)	24	0	0	0
HZSM-5 (41–55; 0.1)	157	0	–	0
Cr/SiO_2 (28; 0.4)	0.80	20	5.3	1.10
NaX (20; 3.0)	1.80	40	0.8	0.30
K/SiO_2 (<20; ~4)	0.10	0	0.15	0
K_2WO_4/SiO_2 (<20; ~4)	0.25	0	0.3	0
MgO (16; 3.9)	0.05	16	0.8	0.13
W/Al_2O_3 (36; 1.0)	60	34	300	102
γ-Al_2O_3 (34; 2.3 and 41; 0.2)**	118	36	256	92
0.6 Na/Al_2O_3 (27; 2.0)	0.90	88	2.3	2.00
K/Al_2O_3 (29; 1.3)	0.60	98	2.3	2.20
$K_2/WO_4/Al_2O_3$ (31; 0.5)	0.30	99	3.0	3.00

* The heats of CO adsorption (Q_{CO}, kJ/mol), which characterize the strength of L-sites, and their concentrations in μmol/m^2 are given in parentheses. The figure before Na indicates its concentration in the catalyst in wt %.

** Two types of sites.

alysts, H_2S is not activated because it is adsorbed only associatively [15, 16]. However, on the K_2CO_3/SiO_2 and K_2WO_4/SiO_2 catalysts that have weak L-sites and very strong basic sites, H_2S undergoes deep decomposition to OH and S^{2-} groups [15]. It is likely that, because of this, thiols are not formed on these catalysts. On the other catalysts with paired sites of a certain strength (Lewis acid and basic sites), the dissociative adsorption of H_2S takes place with the formation of reactive SH^- structures [11], whose reaction with RO groups results in a thiol. The surface of Al_2O_3 modified with alkaline additives contains a considerable amount of SH groups. Therefore, these catalysts are selective in the formation of alkanethiols; however, the catalysts exhibit a low activity because of the presence of weak L-sites.

Thus, we can conclude that proton-donor catalysts or SiO_2 modified with an alkali cannot be used in the thiolation of propanol and butanol because only alcohol dehydration rather than thiolation occurs in the presence of these catalysts. These results are different from our previous data [1, 11] on methanol conversion. In the interaction of methanol with H_2S in the presence of acid–base catalysts, the thiolation reaction with the formation of methanethiol and dimethyl sulfide primarily occurred. The dehydration of methanol with the release of dimethyl ether occurred only to a small extent under specific conditions. On catalysts with strong acid sites, the initially formed methanethiol was converted into dimethyl sulfide as a result of condensation or reaction with another methanol molecule. In the case of propanol or butanol conversion on catalysts with strong proton sites, even with a very large excess of H_2S, the alcohols underwent only dehydration, mainly, with the release of alkenes. The formation of alkanethiols or dialkyl sulfides did not occur. On catalysts with strong L-sites, alkanethiols were obtained in low yields, whereas dialkyl sulfides were not formed at all. Further studies are required to explain the above differences in the behaviors of methanol and its homologues. Common to methanol, propanol, and butanol is that a catalyst that contains paired sites (Lewis acid sites and basic sites) of certain strength is active in the formation of alkanethiols. Aluminum oxide modified with alkaline additives is the best suited catalyst for the preparation of alkanethiols. Although this catalyst exhibits a low activity, it is highly selective in the formation of thiols.

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