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# ACTIVITY OF CATALYSTS IN 1-BUTANOL REACTION WITH $H_2S$

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Reaction of 1-butanol with $H_2S$ has been studied at 300 $^{o}C$ and 0.1 MPa on catalysts of various composition. The catalysts that contain mainly strong proton sites on their surface accelerate dehydration of alcohol alone. In the presence of catalysts possessing acidic and basic Lewis sites 1-butanethiol is formed. Reaction rate increases as the concentration and strength of Lewis acid sites increase.

## INTRODUCTION

There are few data concerning the catalytic reaction of $H_2S$ with saturated alcohol [1]. We now present a study on 1-butanol reaction with $H_2S$ in the presence of catalysts differing in their acid-base surface properties.

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**EXPERIMENTAL**

As catalysts we used $\gamma$-$Al_2O_3$ (trade mark A-1), commercial MgO, zeolite NaX and decationed high silica zeolite HZSM-5 (Si/Al=100) as well as samples supported on $SiO_2$ and $Al_2O_3$ and containing 25% of $H_4SiW_{12}O_4$ (sample HSiW/$SiO_2$), 1.5% of $Cr_2O_3$ (sample Cr/$Al_2O_3$), 5% of KOH (sample K/$SiO_2$ and sample K/$Al_2O_3$). Catalyst preparation procedure is described elsewhere [2]. Their acid-base properties are given in [1,2].

We used $H_2S$ of 99.5% purity obtained via $H_2$ interaction with S on an Al/Ni/Mo catalyst. 1-Butanol was a commercial product (chemically pure grade).

We performed experiments in a flow circulating set-up at atmospheric pressure and T= 300 $^{o}C$. We saturated helium with butanol in a thermostated saturator and then mixed it with a $H_2S$ flow supplied from a vessel. Then the mixture came to a heated reactor filled with 0.25-0.5 mm catalyst particles. A circulating pump agitated the mixture, the circulation number being 400 L/h. The whole system was thermostated at 150±10 $^{o}C$. We analyzed reagents and products obtained by an LKhM-8MD chromatograph provided with a catharometer (fixed phase Porapaque Q and R (1:1), column size 2mx3mm, detector current 150 mA, temperature 140-220 $^{o}C$, the rate of temperature increase 25 $^{o}C$ per min). In each run we used a fresh catalyst sample of certain weight. Experiment ran for 1 h. According to analysis results we determined butanol conversion X (%), product yields with respect to converted butanol (selectivity S, %) and reaction rate W with respect to unit catalyst surface ($\mu mol/m^2$ h) or with respect to one Lewis acid site (mmol/h) at X=70 %, except for MgO and K/$SiO_2$, when X= 60 and 20 %, respectively.

**RESULTS AND DISCUSSION**

Therefore we have studied the catalysts' activity at T= 300 $^{o}$C, P= 0.1 MPa, initial butanol concentration 1.4 vol.%, and that of $H_2S$ being 14 vol.%.

We have previously proved that no reaction occurs without a catalyst. The catalyst introduction accelerates the reaction (see Table). We have also found that the rate and direction of the reaction depend on the catalyst composition. Thus on HZSM-5 and $HSiW/SiO_2$ the reaction starts at small $\tau$ equal to 0.003 and 0.04 s, respectively. As $\tau$ increases to 0.045 and 0.3 s, respectively, butanol is converted completely. However, on both catalysts only butanol dehydration occurs, producing 1- and 2-butenes, but no sulfur-containing products form. The selectivity towards butenes does not change as X increases even at large $\tau$ equal to 1 and 5.4 s for HZSM-5 and $HSiW/SiO_2$, respectively. Therefore, butenes do not undergo further conversions including those with $H_2S$. However, butanol conversion on the above catalysts occurs at a high rate (W= 80-90 $\mu mol/m^2 \cdot h$).

$K/SiO_2$ also accelerates butanol dehydration alone but proceeds far slower (W= 0.6 $\mu mol/m^2 \cdot h$). Butanol conversion grows as t increases from 4.5 to 13.5 s but does not exceed 30%.

On $Cr/SiO_2$, MgO, NaX, $Al_2O_3$, $K/Al_2O_3$ catalysts 1-butanethiol forms beside butenes. Butanol conversion appears to grow as $\tau$ increases, but the selectivity towards butanethiol and butenes does not depend on X (see the Table). Thus butanethiol and butenes form from butanol independently:

$$C_4H_9OH \begin{cases} \longrightarrow C_4H_9SH + H_2O \\ \longrightarrow C_4H_8 + H_2O \end{cases}$$

Among the catalysts mentioned $K/Al_2O_3$ appears to be the most selective towards butanethiol (S= 92-98 %). For other catalysts S is lower and lies within 16-40 %.

On $\gamma$-$Al_2O_3$ the specific rate of butanol conversion is very high (W= 590 $\mu$mol/$m^2$ h). On HZSM-5 and $HSiW/SiO_2$ it is lower by 1 order, on all other catalysts by 2-3 orders of magnitude.

We can ascribe the features observed to the acid-base properties of our catalysts.

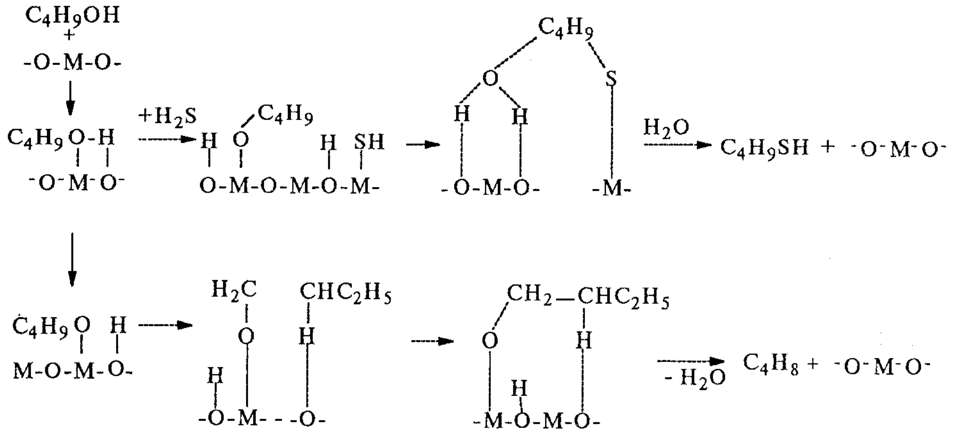
According to [3,4], alcohol dehydration involves the acid sites of catalysts. It goes through a stage producing alkoxide structures that are then converted with alkene elimination. The dehydration rate increases as the strength of acid sites increases [5]. Most probably that is why catalysts with strong proton sites (HZSM-5, $HSiW/SiO_2$) and those with strong Lewis acid sites ($\gamma$-$Al_2O_3$) provide high rates of butanol conversion. We think that on $Al_2O_3$ the reaction rate is so high because butanol activation occurs easier when the conjugated Lewis acid and basic sites work together.

In the presence of $H_2S$ the alkoxide species formed on alcohol adsorption is converted to produce thiol. $H_2S$ activation most likely occurring through HS-structures favors the process [1].

On proton donating catalysts $H_2S$ is not activated [6,7]. This explains the fact that there is no butanethiol in butanol conversion on HZSM-5 and $HSiW/SiO_2$. On $K/SiO_2$ having weak Lewis and strong basic sites $H_2S$ is converted to $HO^-$ and $S^{2-}$, which hinders thiol formation.

On other catalysts with pair sites (Lewis acid and basic sites) a dissociative chemisorption of $H_2S$ occurs to produce reactive $HS^-$ species [1]. This favor butanethiol formation on such catalysts.

Taking into account data on the adsorption of alcohols and $H_2S$, we can suggest the following scheme of butanol conversion in $H_2S$ on the above catalysts:



The rate of overall butanol conversion referred to a single Lewis site ($W_L$) increases with the strength of these sites ($Q_{CO}$):

| | $\gamma$-$Al_2O_3$ | $K/Al_2O_3$ | $Cr/SiO_2$ | NaX | $K/SiO_2$ | MgO |
|---|---|---|---|---|---|---|
| $Q_{CO}$ (kJ/mol) | 34 | 31 | 28 | 20 | ~18 | 16 |
| $W_L$ (μmol/h) | 250 | 3 | 5 | 1 | 0.3 | 0.8 |

This fact confirms that Lewis acid sites are important for butanol conversion. Some of our catalysts contain basic sites as well, but we have failed to follow how these basic sites affect butanol conversion.

**Table 1**

1-butanol conversion in $H_2S$ medium at T= 300 $^oC$

| τ (s) | X (%) | Selectivity (%) | | τ (s) | X (%) | Selectivity (%) | |
|---|---|---|---|---|---|---|---|
| | | $C_4H_9SH$ | $C_4H_8$ | | | $C_4H_9SH$ | $C_4H_8$ |
| | | $\gamma$-$Al_2O_3$ | | | | NaX | |
| 0.01 | 39 | 25 | 70 | 0.4 | 27 | 33 | 63 |
| 0.015 | 50 | 36 | 64 | 0.7 | 50 | 40 | 56 |
| 0.02 | 68 | 43 | 63 | 1.5 | 72 | 40 | 56 |
| 0.03 | 77 | 35 | 65 | 2.1 | 83 | 42 | 60 |
| 0.05 | 90 | 36 | 62 | | | | |
| 0.12 | 100 | 36 | 64 | | | | |
| | | $K/Al_2O_3$ | | | | MgO | |
| 1.2 | 30 | 92 | 5 | 1.9 | 23 | 13 | 83 |
| 1.7 | 40 | 97 | 3 | 7.7 | 40 | 18 | 84 |
| 2.6 | 55 | 98 | 2 | 14.0 | 50 | 14 | 84 |
| 3.5 | 58 | 97 | 3 | 21.0 | 62 | 16 | 81 |
| 5.2 | 75 | 93 | 4 | | | | |
| 6.1 | 79 | 92 | 4 | | | $Cr/SiO_2$ | |
| 8.7 | 92 | 97 | 3 | | | | |
| 10.4 | 93 | 94 | 5 | 0.4 | 20 | 17 | 80 |
| 12.1 | 95 | 95 | 5 | 0.9 | 37 | 19 | 76 |
| | | | | 2.5 | 58 | 21 | 76 |
| | | | | 4.3 | 80 | 20 | 80 |
| | | | | 7.9 | 92 | 23 | 78 |

**REFERENCES**


1. A.V.Mashkina: *Sulfur Report*, **10**, 279 (1991).
2. A.V.Mashkina, E.A.Paukshtis, V.N.Yakovleva: *Kinet. Katal.*, **29**, 596 (1988).
3. V.B.Kazanskii: *Usp. Khim.*, **57**, 1937 (1988).
4. O.V.Krylov, V.A.Matyshak: *Usp. Khim.*, **63**, 585 (1994).
5. L.V.Malysheva, N.I.Kotsarenko, E.A.Paukshtis: *React. Kinet. Catal. Lett.*, **16**, 365 (1981).
6. I.V.Desyatov, E.A.Paukshtis, A.V.Mashkina: *React. Kinet. Catal. Lett.*, **41**, 161 (1990).
7. V.M.Mastikhin, I.L.Mudrakovskii, A.V.Nosov A.V.Mashkina: *J.Chem. Soc. Catal. Lett. Farad. Trans. I.*, **85**, 2819 (1989).